TREATMENT OF PHENOLIC WATER USING ADSORPTION

A Project submitted to the
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By

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UNDER THE GUIDANCE

OF

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MAY- 2011

CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled "**TREATMENT OF PHENOLIC WASTEWATER USING ADSORPTION**" in the partial fulfilment of the requirements of the award of the degree of **Master of Technology** in **Chemical Engineering,** submitted in the Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, is an authentic record of my own work carried out during the period of July 2010 to April 2011 under the supervision of **Dr. A. Kumar**, Assistant Professor, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date: May 2011 **(PRATEEK KHARE)**

Place: Rourkela

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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PRATEEK KHARE

ABSTRACT

In the present study the adsorbent was prepared from the fruit's of Terminalia Chebula obtained from local area of NIT Rourkela. The adsorbent was characterized for BET surface area, point of zero charge, CHNS, SEM, EDX, FTIR etc. The feasibility of using Terminalia Chebula activated carbon (TCAC) were investigated and optimized. The pH =5.5 was observed optimum pH for the maximum removal of phenol. The equilibrium adsorption data of phenol showed good correlated to Freundlich and Redlich-Peterson isotherm models. Adsorption kinetic data represents to the pseudo second order kinetic model. The maximum uptake capacity of phenol on to TCAC was found 36.77 mg/g at 303K the negative value of $\Delta G < 0$ showed the process is spontaneous. The Taguchi experimental design was used to optimize the process variable for Phenol –TCAC system.

KEYWORDS: - Phenol, TCAC, Adsorption, Taguchi

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List of figures and Tables

Nomenclature

C_t	Final concentration in mg/l at any time t
C_0	Initial concentration in mg/l at any time t=0.
m	Mass of the TCAC in g.
q_{eq}	Amount of Phenol adsorbed at equilibrium
V	Volume in ml of adsorbate solution.
K_1	Rate constant of pseudo-first order adsorption.
K_2	The pseudo-second order is rate constant of Phenol adsorption.
q_{eq}	The amount of Phenol adsorbed at equilibrium
q	The amount of Phenol is adsorbed at time *t* (min)
β	Exponent ($0<\beta<1$) (in Redlich-Peterson isotherm)
ΔS	Change in the entropy for active complex formation, k J/mol
ΔH	Enthalpy for active complex formation, kJ/mol
ΔG	Gibbs free energy for active complex formation, J/mol
ΔS^o	Change in the entropy for adsorption, J/mol
ΔH^o	Enthalpy of adsorption, J/mol
ΔG^o	Gibbs free energy of adsorption, J/mol
ρ	Density, kg/m^3
K_f	Freundlich constant (mg/g).
BT, A_T	Temkin constants.
K_R	Redlich–Peterson constant (l/g).
a_R	Redlich–Peterson constant having unit of (l/mg).
β	Exponent that lies between 0 and 1, Redlich Peterson
AR	Analytical grade
TCAC	Terminalia chebula activated carbon
BET	Brunauer–Emmett–Teller
SEM	Scanning Electron Microscopy
AR	Analytical grade
TCAC	Terminalia chebula activated carbon

Chapter-1

INTRODUCTION

1 INTRODUCTION

Due to fast depletion of the freshwater resources, the world is facing crisis of fresh water all over the world. The industrial and domestic activities have polluted the surface water as well as ground water up to a greater extent (Armour, 1991). Hence the cost of removal of organic pollutants from water has been increases remarkably in last few years. There are several technologies for treating wastewaters (Busca et al, 2008). And this poses a great challenge to chemical engineer's to develop low, cost effective and environmentally safe disposal and treatment methods.

Apart from other organic and inorganic pollutants, the presence of phenol and their derivatives also contribute to pollute water. The US Environmental Protection Agency (EPA, 1984) had classified the Phenolic compounds as high priority pollutants due to their extensive impact on the deterioration of the water environment. The industries like leather, paint, pharmaceutical, coking plant petrochemical, oil refinery, plastic, explosives, steel, pesticides etc and others uses phenolic and its derivative compounds as their products and raw materials (Busca et al, 2008). The toxic and hazardous nature of phenols and their derivatives have been well documented (Denizli et al., 2004). The high concentration discharge of these compounds in water receiving bodies and their exposure over a long period can cause severe impact on environment. The exposure of phenol and its derivative compounds to human and animals causes liver and kidney damage, central nervous system impairment, diarrhea and excretion of dark urine (Sarkar and Acharya, 2006, OO Olujimi et. al., 2010). However detailed information about the phenol is given in appendix.

Several treatment methods are available for treating the organic waste include granular activated carbon processes and reverse osmosis, anaerobic processes, the electro Fenton method, and combined applications of flotation and coagulation processes, stripping and oxidation has been tabulate in table 1.1 (Busca et al, 2008). All of these are used for treating organic and inorganic waste. Most of these methods suffer from some drawbacks, such as high capital and operational cost, regeneration cost, and problem of residual disposal. Liquid phase adsorption has been shown to be a highly efficient, well-established technique for the removal of organic compounds due to its simplicity, adsorbent cost, effectiveness and the availability of a wide range of adsorbents (Salame and Bandosz, 2003). Activated carbon is often the preferred as an adsorbent for the removal of organic compounds due to its high adsorption capacity. However, it suffers

Table 1 Different technologies for the removal of wastewater for phenol pollutant (Busca et al, 2008)

Technique	Temperature Range (°C)	Condition (Pressure and pH)	Reactor	Additional chemicals	Performances (ex.)	Comments
Distillation	95–180	~1 atm, As such	Distillation column	No	Complete separation possible	Commercial;recovery of phenol; costly
Liquid–liquid extraction	I 20–50; II 60–180 (regeneration)	~1 atm, As such	I washing column; II distillation column	DIPE or MIBK (recycled)	kd (WpH in MIBK/ WpH in H2O)~ 100at 30 °C	Commercial, second -ary pollution(disposal or burning of spent AC
Adsorption (AC)	20–50	~1 atm, Neutral	Fixed bed column	AC	Adsorption capacity 200–400 mg_{ph}/g_{AC}	Commercial,secondary pollution disposal or burning of the spent AC adsorbent)
Adsorption (resins, inorganics)	I 20–50; II 20–50 (regeneration)	~1 atm neutral	Fixed bed column	PV-PDS resin; egenerat -ion solution	Adsorption capacity 80–100 mg_{ph}/g_{AC} (resins); adsorption Capacity <200 mg_{ph}/g_{AC} (silicalite)	Commercial, secondary pollution (regeneration solution); possible recovery of phenol
Pervaporation	20–50	~1 atm/1–20 Torr As such	Membrane module	Membrane	PEBA: enrichment factor 4–60 permeate flux 0–0.3 $kg_{ph}/(m^2 h)$	Commercial, recovery of phenol
Membrane extraction (ex.MTBE)	20–50	~1 atm as such	Membrane module	Membrane Solvent	C_0 0–5 g/l; feed ph flow 1–8 m^3/s; depletion degree 50–100% MTBE)	Commercial, recovery of Phenol
WAO	180–315	20–160 Atm Slightly acidic	Bubble column, stirred reactor, jet-agitated reactor	Air, an acid	COD° 10–100 g/l, 15–120 min, COD conv 75–90%	Commercial, further treatment needed
SWAO	400–650	250–350 Atm As such	Bubble column, stirred or jet-agitated reactor	Air	TOC conv 99.99%; residual TOC < 3.5 ppm	Comercial, total combustion possible
CWAO	100–200	3–35 Atm As such	Pressurized slurry TR; fixed trickle bed	Air/catalyst	Noble metal or metal oxide cat.; COD° 10–100 g/l, TOC conv > 80–99%; t > 20 min	Commercial; Total combustion possible; Catalyst leaching?

from some drawbacks, such as high cost and the irreversible nature of adsorption. Thus, the requirement of low cost adsorbent comes here which fulfill all the properties of activated carbon but at the expense of low cost the comparison of cost of activated carbon is given in table 1.2.

Table 1.2List of cost of various adsorbent (Busca et al, 2008).

Adsorbent	Cost (US$/kg)
AC	20–22
Natural zeolite	0.03–0.12
Coal	0.19–0.15
Red mud	0.025
BFA	0.02
Carbonaceous adsorbent	0.1
Clay	0.04–0.12

The different alternative feed stocks of waste material which were rigorously characterizes in table1. 3.

1.1 Activated carbon

Activated carbon is a porous material which is commercially used for the removal of liquids and gaseous pollutants as well for the gas storage application because of its large surface area. It is carbonaceous adsorbent and has highly amorphous structure (Bansal and Goyal, 2005). There are several factors on which the effectiveness of adsorption process depends these adsorption conditions may be the nature of the adsorbent (acidic/ basic), the characteristics of adsorbent which includes the high surface area, pore size distribution, ash content and hydrophobicity. These characteristics defined the concentration of carbon atoms in the matrix, and the density and type of functional groups present on the surface (Boehm, 1966). The acidity or basicity of the activated carbon depend upon the presence of heteroatom's such as oxygen, which can form phenols, ethers, lactones ketone, carboxyl and nitrogen in the form of amines and nitro groups; and phosphorus as a phosphate can determine (Puri, 1970). On the other hand, adsorption also depends on the nature of the adsorbate depends on its hydrophobicity, polarity, and size of the molecule. The nature of the functional group present important factors is to be determined before

the selection of adsorbent (Terzyk, 2003). There are several agricultural waste materials such as waste apple pulp

Table 1.3 Alternative feed stocks proposed for preparing activated carbon and low-cost adsorbents used in wastewater treatment (Mohan and Singh, 2005).

Alternative feed stocks		
Bones	Fertilizer waste slurry	Petroleum acid sludge
Bagasse	Fish	Pulp-mill waste
Bark	Fruit pits	Palm tree cobs
Beat-sugar sludge	Graphite	Petroleum coke
Blood	Jute stick	Petroleum acid sludge
Blue dust	Kelp and seaweed	Potassium ferrocynide residue
Carbohydrates	Lignin	Rubber waste
Cereals	Lignite	Rice hulls
Coal	Lampblack	Refinery waste
Coffee beans	Leather waste	Reffination earth
Coconut shell	Municipal waste	Scrap tires
Coconut coir	Molasses	Sunflower seeds
Cottonseed hulls	Nut shells	Spent Fuller's earth
Corncobs	News paper	Tea leaves
Distillery waste	Oil shale	Wheat straw
Fuller's earth	Olive stones	Wood

,straw, coconut shell, coir pith, saw dust, apricot stone shell, olive stones, sugarcane bagasse peanut hull and many others have been employed to produce activated carbons with high surface area. Two main processes are involved in the production of activated carbons

a) Carbonization of precursor material ($< 800°C$)
b) Activation (using activating agent) of resulting carbonized substances

The porosity of raw material can be increased by activation process, which can be done by physical activation and chemical activation. The physical activation involves oxidation and gasification of the char at high temperatures greater than ($800°C$). While the chemical activation process is carried out in a single step by the thermal decomposition of the raw material impregnated with certain chemicals such as HCl, H_2SO_4, $MgCl_2$, NaOH, KOH, $ZnCl_2$, NH4Cl, $BaCl_2$, K_2CO_3, K_2HPO_4 and H_3PO_4. The temperatures used in chemical activation are lower than that used in the physical activation process. Although physical activation permits better control over the creation of a desired micro porous structure, chemical activation is an adequate procedure to develop large pores in activated carbons (Anirudhan, et al., 2009). In the present work, a new type of agricultural waste has been used (seed waste of Terminalia chebula fruits a Ayurvedic plant for the preparation of adsorbent for treating phenolic wastewaters.

1.2 Taguchi experimental design for optimizing the process variables

The Taguchi optimization approach is a robust tool for Design of Experiments (DOE). The robustness means that it increases the quality of the product reduces cost and also at the same time reduce the time required for experimental investigation. This approach is totally based on statistical design of experiment and derived by a Japanese scientist Taguchi (Park, 1996). Taguchi proposed that the engineering optimization of a process or product should be carried out in a three step approach: system design, parameter design and tolerance design. The most important step in the design of an experiment lies in the selection of control factors. Taguchi creates a standard orthogonal array to accommodate these requirements. Depending on the number of factors and levels needed, the choice is left to the user to select the standard orthogonal array. The orthogonal arrays (OAs) differentiate Taguchi's approach from the other statistical approach (Madaeni et. al., 2006). In OAs parameters and levels are taken in such a way, for each level of any parameter, all levels of other parameter occurs at equal number of times, which gives a balanced design. As compared to a full factorial design, the number of

experiments in Taguchi's technique is substantially reduced. For the selection of a particular OA, the number of parameters, the number of levels and their possible interactions must be taken into consideration. Thus, Orthogonal arrays (OAs) were originally developed by Taguchi to control experimental error (Singh, et. al., 2002).

1.3. OBJECTIVES OF THE PRESENT WORK

- Development of low cost adsorbent from agro waste.
- Characterization of laboratory prepared adsorbent for its valuable adsorbable properties such as surface area, point of zero charge, CHNS, FTIR and SEM.
- Kinetics and equilibrium study of the phenol- TCAC (Terminalia Chebula Activated Carbon) system.
- Comparison of adsorption capacity of phenol with others low cost adsorbents available in literature.
- Optimization of experimental parameters using Taguchi experimental design.

Chapter-2

LITERATURE REVIEW

2. Literature review

Last 3-4 decades many authors have tried different methods for the preparation of activated carbon. As discussed earlier in brief about the factor on which the feasibility of activated carbon depends and which mainly depends on the methods of preparation of activated carbon. The agricultural waste producing around the world in huge quantity; hence the manufacturing of activated carbon from such agro waste is the cheap and suitable procedure in the current context.

There are two methods which can be used for the preparation of adsorbents the from the raw agro waste materials: either Gasification or by Pyrolysis (Putun et al, 2005). The pyrolysis is a suitable process because it produces energy, char, oil and gaseous product. However, it can further be divide two parts based of activation process. The systematic scheme for the preparation of activated carbon is presented below

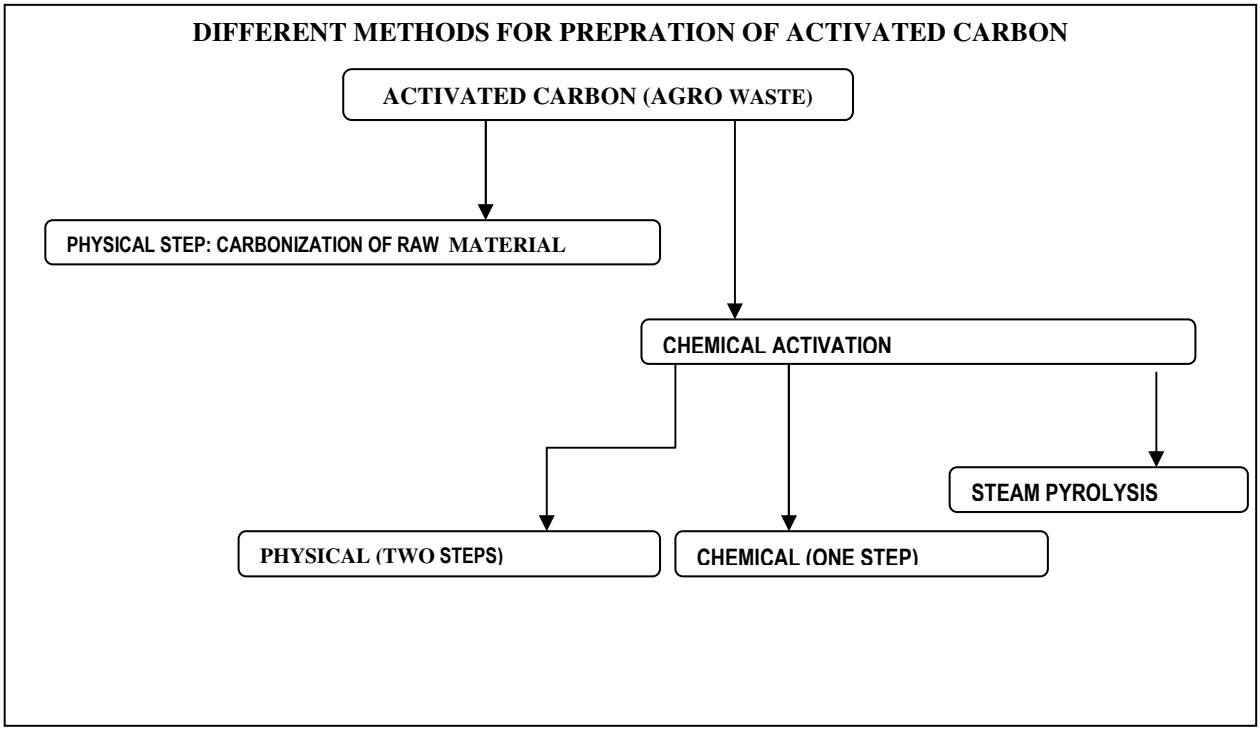

Fig. 2.1 Different routes for the preparation of activated carbon.

2.1 Physical activation step.

In this classification the pyrolysis i.e. the carbonization of raw materials was performed in absence of oxygen or air at the certain heating rate keeping the temperature below 800-700 °C. Many authors used different raw materials that were listed in table 1.3 (Mohan and Singh, 2005, Pollard et al., 1992) for the preparation of activated carbon. Alhamed, (2006), studied the yield and quality of activated carbon prepared from date's stones for the removal of methylene blue and phenol pollutants from water. The pretreatment of raw materials was done with $ZnCl_2$ at different ration of solid to $ZnCl_2$ solution. R is equal to the ratio of zinc chloride to dry dates' stones. The results showed that for phenol R value (0.5) give the best result while for methylene blue R value was 2. The optimum condition was obtained for phenol: The maximum unit capacity for phenol was 19 mg/g at Ct = 3 hours and CT (carbonization temperature) = 600 °C and the corresponding AC yield was 47.3%. On other hand, milder conditions (Ct (time to reach equilibrium) = 0.5 h and CT = 500℃) were required to produce AC with maximum capacity for phenol removal of 75.0 mg/g and AC yield of 64.6%, while for MB was 148 mg/g at carbonization time (Ct) = 1 hour and carbonization temperature (CT) = 600 °C and the corresponding yield was 32%. Milder conditions (Ct = 0.5 h and CT = 500 °C) were required to produce AC with maximum capacity of 286.3 mg/g with a yield of 31%. Hence the $ZnCl_2$ had given the best results with methyl blue as compare to phenol removal.

Shawabkeh and Abu-Nameh, (2007) had prepared the activated carbon by pretreating the pecan shell with phosphoric acid followed by sodium dodecyl sulphate for the removal of phenol and methylene blue. For the phenol surfactant suppress the phenol removal efficiency. While on the other hand the maximum uptake of activated carbon for dye was 98 %. The sorption capacity of 410 mg/g was obtained at pH 9 and for phenol 18 mg/g at pH 11 for initial concentration 35 mg/l. Uddin et al, (2007) had performed the batch adsorption study for the removal of phenol from aqueous solution using water hyacinth ash as an adsorbent. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, initial phenol concentration, contact time and adsorbent dosage. The maximum uptake of phenol took place at a pH in the range of 2.5-5 and further the adsorption of phenol decreased with increasing pH. Equilibrium data fitted very well in a Langmuir isotherm equation, confirming the monolayer sorption with higher correlation coefficient value. The maximum uptake capacity of phenol onto water hyacinth ash was obtained 30.49 mg/l. The pseudo-first-order and pseudo-second-order

kinetic models were used to analyze the data obtained for phenol adsorption onto water hyacinth ash.

Vazquez et al, (2007), had investigated the batch adsorption kinetics of Phenol adsorption by Pinus. pinaster bark pre-treated with formaldehyde in acid medium . The results showed with increasing the solid/liquid ratio, the percentage of phenol removal increased and with decreasing the initial phenol concentration and the pH. Phenol adsorption has been described using a kinetic model based on the control of mass transfer within the pores of the bark, which has allowed determining the diffusion coefficients for the higher concentrations essayed. Adsorption equilibrium data have been fitted satisfactorily by BET and Freundlich isotherms primarily for lower concentration of phenol.

Panumati et al., (2008), had prepared activated carbons using different raw materials like, bagasse (B), oil palm shell (OP) and pericarp of rubber fruit (PR). The obtained activated carbons were characterized for iodine number, BET surface area, surface functional groups, and point of zero charge (pH pzc). The iodine number and BET surface area for B, OP and PR 939, 808, and 868 (mg/g), while surface area were 1076, 770 and 877 (m2/g) respectively. Adsorption study of phenol in aqueous solution at pH 2 and pH 12 were also determined. The adsorption data were fitted to Freundlich isotherm. Adsorption capacity of phenol at pH 2 is greater than at pH 12. Since at pH 2 the surfaces of activated carbons are protonated and have acidic surfaces with positive charges. Phenol behaves as a weak base that interacts with the acidic surface of activated carbons by dispersion electron donor-acceptor interaction. The adsorption capacity of phenol of the different types of activated carbon was approximately the same.

Anirudhan, et al., (2009), used a biomass waste from coir industry for the prepation of activated carbon by chemical activation method (H_3PO_4). The efficacy of activated carbon using for the removal of phenol (P), p-chlorophenol (PCP) and pnitrophenol (PNP) from water and petroleum refinery industry effluents was investigated. The effects of contact time, adsorbent dose, ionic strength and initial concentration on the adsorption of phenols onto the activated carbon were investigated. The optimum pH for the maximum removal of phenols was 6.0. The equilibrium adsorption data of phenols were correlated to Langmuir and Freundlich isotherm models, the latter being the best fit of the experimental data. The kinetics of the adsorption process and mass transfer were investigated using McKay and Urano-Tachikawa models. Adsorption kinetic data

fits the Urano-Tachikawa kinetic model. The adsorbed phenols can be recovered by treatment with 0.1 M NaOH solution. Though, the physical activation method will provided the porous surface whose surface area ranging from 200- 700 mm^2/g.

El-Naas et al., (2010), had carried out batch adsorption experiment to evaluate the effectiveness of activated carbon locally prepared from date-pits and are used for the removal of phenol from refinery and synthetically prepared aqueous solution wastewater. Different kinetics and isotherm models were tested to fitted to equilibrium and kinetics data for the adsorption of phenol. Kinetics data were best fitted to the pseudo second order model, and the equilibrium data to the Sips isotherm. High regeneration efficiency was achieved using pure ethanol more than 86% regeneration efficiency after four regeneration cycles. The results show that the capacity of DP-AC is comparable to other adsorbents, which proves that it can be effective as a low-cost alternative to commercial activated carbons for the removal of phenols from wastewater. And also, the utilization of DP can provide an excellent disposal option for the date palm industry.

2.2 Chemical activation step

In this classification, the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants. Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, However, a two-step process (an admixed method of physical and chemical processes) have been reported by many authors, which has been described below . The most common chemical agents are $ZnCl_2$, KOH, H_3PO_4 and less K_2CO_3.

Dursun et al., (2005) was used the beet pulp, a major low value by-product in sugar industry was used to prepare carbon for phenol adsorption. It was produced by carbonization in N_2 atmosphere at 600 $°C$ for 1.5 h. The surface area of beet pulp carbon was measured as 47.5m^2 g^{-1} by using BET method. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, temperature and initial phenol concentration. The optimum pH value was found to be 6.0. The results showed that phenol adsorption increased with temperatures up to 60 $°C$ and initial phenol concentrations up to 500 g dm^{-3}. Kennedy et al., (2007), prepared the activated carbon from rice husk by two stage activation method. The chemical activation at 900 $°C$ was found to be the optimum among 700, 800 and 900$°C$. The results showed that two steps

produced highly porous and high pore volume and surface area. The maximum uptake was found to be 2.35×10^{-4} mol/g at 20 $°C$ and final pH 2.7 and the surface area was 438.9 m^2/g at CT 900$°C$.

Mourao et al., (2006) had prepared Activated carbons from solid cork wastes by physical activation with carbon dioxide or steam, and followed by chemical activation by impregnation with phosphoric acid. The results showed that physical activation preferably with water vapour appears to be the most effective preparation method as it leads to materials with narrow pores, and hence strongly enhanced adsorption at low concentrations, and reasonably high pore volumes.

Sricharoenchaikul et al., (2008) had prepared activated carbon from pyrolyzed physic nut waste. The results showed that depending upon the chemical activation method the high carbon contents of activated materials 90.3%, mesopore of 2–50 nm and total pore volumes of the materials were also significantly enhanced. The activated carbon prepared by chemical activation of the pyrolyzed physic nut residue at 800 $°C$ with KOH attained a maximum BET surface area of 532.3 m^2 /g, while the surface area of those activated with H_3PO_4 and CO_2 were lower. FTIR analysis of pyrolyzed char indicated that functional groups on each activated carbon are quite similar even with different activation processes. The high value of BET surface area indicated that physic nut residue pyrolyzed at 800 °C and followed by KOH activation could be used as a low-cost adsorbent with favorable surface properties.

Girods et al., (2009), used wood of particleboard waste as a raw material for the synthesis of activated carbon. A two steps thermo-chemical process is used for the preparation of activated carbons from raw material using pyrolysis and steam activation at 800 $°C$. The resultant carbonaceous char having specific surface areas within the range 800–1300m2/g., which showed adsorption capacities of phenol as high as 500 mg/g.

Dash et al., (2010) had prepared activated carbon by Shorea Robusta leaf litter. A nonconventional material was impregnated with phosphoric acid, used for the reduction of Zinc and Copper metal ions from aqueous phase.

Figueiredo et al., (2011), had studied the influence on texture and surface chemistry on the phenol adsorption capacity by activated carbon fibers (ACFs). ACFs were prepared by carbonization of a phenolic textile fiber under nitrogen flow, followed by activation with H_2O and CO_2 (under atmospheric pressure and supercritical state). The results showed that BET surface area and pore volume increase significantly as the burn-off increases. Taking into

consideration both the amounts adsorbed and the adsorption rates, CO_2 activated carbon fibres were found to be better adsorbents for phenol than the H_2O activated carbon fibres. The amount of chemisorbed phenol decreases with an increase in surface oxygen concentration.

Kamble et al., (2008), had done the comparative study of phenol and o-chlorophenol on commercial zeolite-Y, fly ash based zeolite (FAZ-Y) and surface modified fly ash based zeolite (SMZ-Y) was studied. It was observed that the adsorption of phenol on SMZ-Y was 4.05 and 3.24 times higher than the FAZ-Y and commercial zeolite-Y, respectively. For O-chlorophenol efficiency was higher than phenol which may be due to the hydrophobicity imparted by surfactant molecules on the surface of fly ash zeolite, consequently leading to organic partitioning.

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Chapter-3

MATERIALS AND METHODS

3.1 Raw material for adsorbent preparation

The fruit's of Terminalia chebula plant commonly known as Vibhitaki in Sanskrit, Bahada in Hindi and Bahera in Oriya. This fruit has an elliptical shape, abrasive seed has enveloped by a fleshy and firm pulp. The pulp part of fruit was used for many ayurvedic medicines (Devi et al., 2005). The solid coating part of the seed was the waste material and is used as a raw material. The raw material Terminalia chebula (TC) i.e. fruits were collected from plants of N.I.T. campus Rourkela, Orissa.

3.2 Adsorbent Preparation

The chars derived from seed coating of Terminalia chebula (TC) wastes have been produced in a pyrolysis reactor as shown in Fig.3.1. The seed coat of the fruit, which has an elliptical shape, abrasive seed has enveloped by a fleshy and firm pulp. This pulp part was used for many ayurvedic medicines (Devi et al., 2005). The solid coating part of the seed was the waste material. It was washed 5-6 times in running tap water and then with distilled water to remove the impurities. Then it was soaked in 2 M HCl solutions for two days and soaked material was sun dried for 24 hrs. The pyrolysis was carried out under the absence of air and in the conditions of heating rate 20 $°C$ /min, temperatures 600$°C$. The reaction was started at 436$°C$ and it would take only 15 to 20 minutes to complete. The char was allowed to cool naturally in reactor. The char was crushed to a desired 100 BSS sieve size particle. The resultant char was then washed with distilled water until the pH of washed water was become neutral.

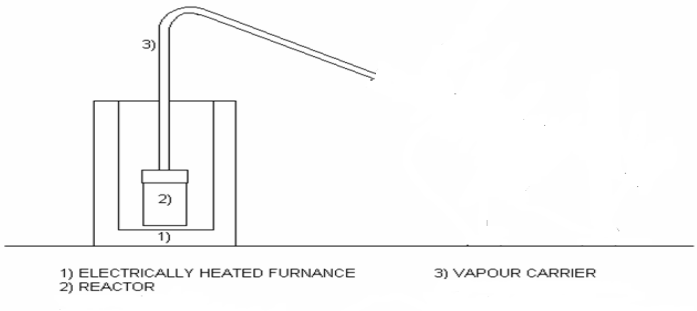


Fig. 3.1 Experimental set up for pyrolysis reactor.

3.3 Reagents and equipment's

All the necessary chemicals used in the study were of analytical grade and obtained from Merck India Limited, Mumbai, India. The Characterizations of the adsorbent was carried out for surface area analysis (Kunash instruments Pvt ltd. Mumbai), Scanning Electron Microscope (SEM) and FTIR studies. The Langmuir and BET surface area were measured by nitrogen adsorption technique for the same adsorbent (TCAC). Scanning electron microscopic (SEM; Model JSM 5410, JELO) study was also conducted to observe the surface texture and porosity of the adsorbent. FTIR (FTIR RX-1, PerkinElmer, USA) spectrometer was employed to determine the type of functional groups in TCAC responsible for Phenol adsorption. UV visible Spectrophotometer (JASCO UV/Vis-550) was used for determination of phenol content respectively in standard and treated solution. The pH of the solution was measured with a 5500 EUTECH pH Meter.

3.4 Preparation of Phenol standards

The stock solution containing 1000 mg/l of standard Phenol was prepared by dissolving 0.25 g of AR grade Phenol in 100 ml double distil (DD) water. After dissolution both the solutions were diluted to 250 ml with DD water in 250 ml volumetric flask. Batch adsorption experiments were performed after proper dilution of stock solution.

3.5 Analytical measurement of phenol

The solution of phenol is colorless. The physical proprieties are illustrated in Table 3.1 (Busca et al, 2008). The standard calibration curve of known concentrations of phenol was ploted by finding out the absorbance at the characteristic wavelength of λ_{max}=270 nm. A spectrophotometer (JASCO UV/Vis-550) is used for the calibration plot, which showed a linear variation up to 100 mg/l concentration. Therefore, the samples with higher concentration of phenol were diluted with distilled water. The standard calibration curve of phenol concentration is shown in Fig. 3.2 with the help of the linear portion of the calibration curve the unknown concentration is determined.

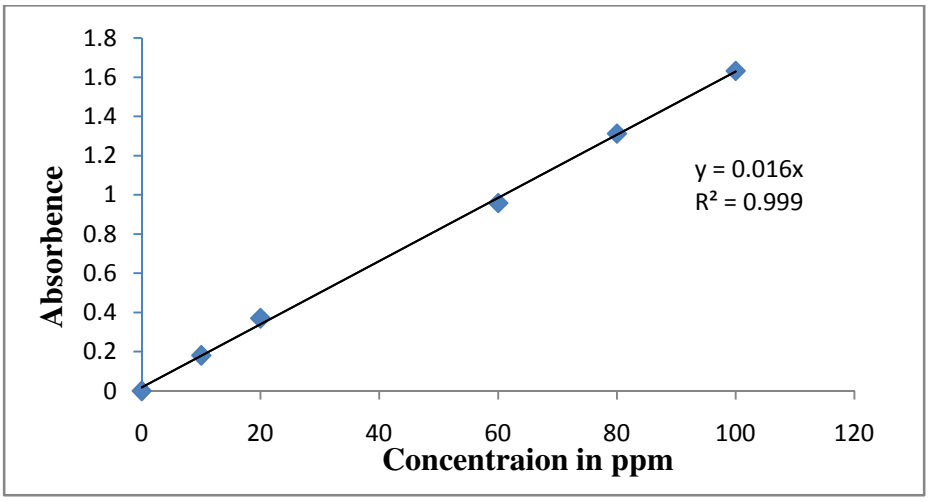
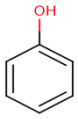


Fig. 3.2 Standard calibration curve of Phenol at different concentration (0-100) mg/l.

Table 3.1 Physical proprieties of Phenol (Busca et al, 2008).

Formula	
Molecular weight (g/mol)	94.11
Tmelt℃	40.9
Tbp℃	181.5
Flash point℃	79
Auto ignition℃	715
Flammability limits in Air (vol%)	1.7 (lower)
	8.6 (higher)

3.6 Surface characterization of TCAC

The surface area and the porous texture of activated carbon were characterized using adsorption BET surface area and SEM. The textural characterization (surface area) of TCAC was determined at -196 ℃ in presence of nitrogen atmosphere. The N_2 adsorption–desorption isotherm was used to determine surface area using the Brunauer–Emmett–Teller (BET) equation. The surface characteristics of samples were analyzed using scanning electron microscopy (SEM) JSM 5410, JELO. Surface morphology is performed in situ on a TCAC powder at different

magnification. Energy dispersive X-ray spectrometer (EDX) of 100 mesh size of TCAC is investigated by semi-quantitative elemental analysis using the energy dispersive X-ray spectrometer of a scanning electron microscope. The ultimate elemental analysis of laboratory prepared TCAC sample is performed by a CHNS Thermo Finnigan Flash EATM 1112 analyzer. Fourier transform infrared spectroscopy (FTIR) Mattson 1000 spectrometer was used in the characterization of the presence of surface functional groups. The absorbance data were processed for the wave number range 4000-400 cm^{-1} using the Essential software. The point of zero charge (PZC) of TCAC was determined using solid addition method.

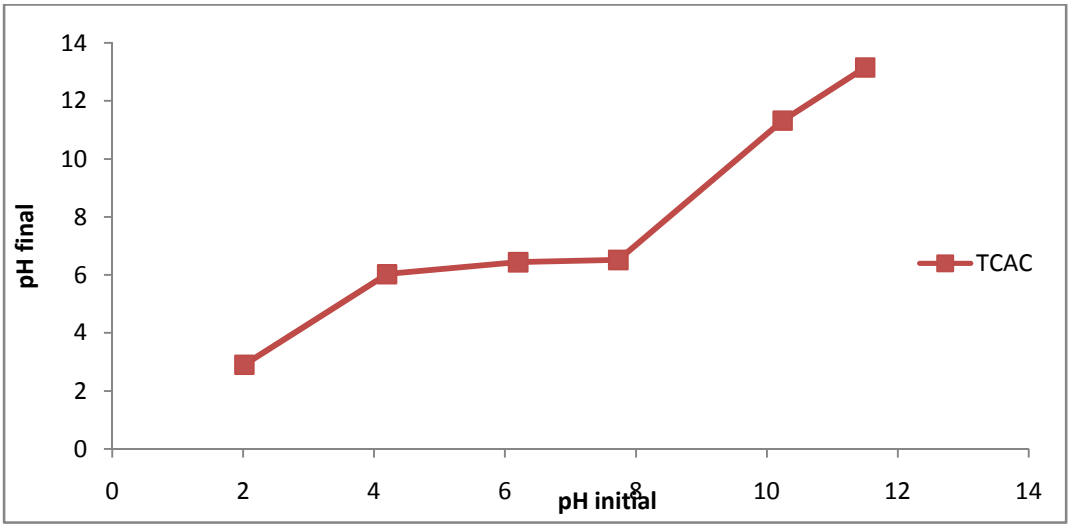


Fig. 3.3 Effect of pH on adsorbent surface (0.15g per 50ml) at 0.1 M KNO3 for 48 hours.

3.7 Batch adsorption procedure

All the batch adsorption experiments were performed on a mechanical shaker equipped with a thermostatic water bath at 120 rpm using 100 ml conical flasks. A series of adsorption experiments were performed at room temperature (30℃). The first experiment was to investigate the effect of adsorbent dose. The different doses of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 g of TCAC was added into the flasks with 50ml solution having Phenol concentration100 mg/l and then agitated for 24 hour at 120 rpm. The pH of the solution was maintained natural.

To elucidate the effect of pH, the experiments were conducted at different pH ranges. The pH of Phenol solutions were adjusted in range (2-12 pH) using HCl (0.03M) and/or NaOH (0.03M)

solutions and then 0.15 g TCAC were added into the series of flask, and then agitated at 120rpm for 24 hours.

50 ml Phenol solution of 100 mg/l and 0.15 g TCAC was added into the series of flasks to investigate the effect of contact time and equilibrium time and then agitated at 120rpm for different time interval ranging from 15 min to 1440 min until the steady state reached.

The effect of initial concentrations for phenol onto TCAC were also studied for different concentrations of phenol 50, 100 and150 mg/l solutions at optimum pH of 5.5 and then treated as the procedure in the first experiment until equilibrium reached. All solution samples were filtered through Whitman 0.45µm filter paper. The concentrations of phenol in treated samples were determined by UV spectrophotometer. The amount of phenol adsorbed per unit mass of the adsorbent was evaluated by using the following equation (3.1)

$$q_e = (C_o - C_t)\frac{V}{m} \tag{3.1}$$

The percent removal of phenol was calculated as follows

$$\%\text{Removal} = \left(\frac{C_o - C_t}{C_o}\right)100 \tag{3.2}$$

Where, C_o is the initial concentration of Phenol, C_t is final concentration in mg/l at any time t, V is volume of solution in ml of adsorbate solution and m is the dose of TCAC in g. All the investigations were carried out two times to avoid any discrepancy in experimental results with the reproducibility.

3.7.1 Kinetic models

The adsorption kinetics of phenol was tested using pseudo-first order, pseudo-second-order, intraparticle diffusion sorption and Bangam equation.

Lagergren proposed a pseudo-first order kinetic model as below. The integrated form of the model

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t \tag{3.3}$$

Where q the amount of phenol is adsorbed at time t (min), q_{eq} is the amount of phenol adsorbed at equilibrium and k_1 is the rate constant of pseudo-first order adsorption.

The adsorption kinetic can also be given by a pseudo-second order reaction. The integrated linearized form of this model was

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{3.4}$$

Where K_2 the pseudo-second order is rate constant of Phenol adsorption. The plot of t/q versus t of Eq. (5) will give a linear relationship, from which q_{eq} and k_2 can be determined from the slope and intercept of the plot, if second order kinetic equation is applicable.

Bangham's equation is represented as in equation (3.5). The plot of $\log\log\left(\frac{C_0}{C_0 - q_t m}\right)$ versus $\log(t)$ gives a linear relationship from which α and k_0 rate constants can be calculated.

$$\log\log\left(\frac{C_0}{C_0 - q_t m}\right) = \log\left(\frac{k_0 m}{2.303 V}\right) + \alpha \log(t) \tag{3.5}$$

Where C_o is the initial concentration of phenol solution, q_t is the adsorption capacity at any time t, m is the adsorbent amount (3 g/l), and V is the volume of the solution.

3.7.2 Adsorption isotherm model

An adsorption isotherm is characterized by certain constant values that express the surface properties and affinity of the adsorbent the adsorption equilibrium data of phenol-TCAC system were analyzed in terms of Langmuir, Freundlich, Temkin, Redlich-Peterson (R-P) isotherm models. The linear forms of different isotherm model are as given below.

Langmuir isotherms are valid for monolayer adsorption onto a surface containing a finite number of identical sites. It is most popular model due to its good agreements with sorption experimental data. Langmuir equation and assumptions (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3.6)$$

The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.

Adsorbed molecules do not interact.

All adsorption occurs through the same mechanism.

At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

Where K_L is the Langmuir adsorption constant (l/mg) related to the energy of adsorption and q q_m signifies adsorption capacity (mg /g).

According to Freundlich isotherm theory (Freundlich, 1906) describes the amount of solute adsorbed onto per gram of sorbent (q_e). It is most widely used and is applicable to adsorption on heterogeneous surfaces. It can be represented in linear form by equation (3.7).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3.7)$$

K_f is the Freundlich constant (mg/g) indicates the relative adsorption capacity of the adsorbent and n the Freundlich exponent indicates the intensity of adsorption. Where K_f and n are constants representing the adsorption capacity and intensity of adsorption respectively. The slope 1/n and intercept K_f is obtained from the plot of Log q_e versus Log C_e.

Temkin isotherm model explicitly accounts for adsorbate-adsorbent interaction. It assumes that fall in heat of adsorption is linear rather than Logarithmic. The equation can be expressed as:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (3.8)$$

Where B_T = RT/b, q_e (mg/g) and C_e (mg/l) are the amount of adsorbed Phenol per unit weight of adsorbent and unadsorbed Phenol concentration in solution at equilibrium, respectively. A_T and B_T are the Temkin constants.

Redlich–Peterson isotherm

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) is an empirical isotherm incorporating three parameters. It is modified from both the Langmuir and Freundlich equations, and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{3.9}$$

Where K_R is the Redlich–Peterson constant (l/g), a_R constant having unit of (l/mg), and β is an exponent that lies between 0 and 1.

3.7.3 Error analysis

Linearization of isotherm and kinetics model somes times resulted inherent biasing. Although there is another rigorous mathematical method called nonlinear regression. (Seidel and Gelbin, 1988). Most commonly, algorithms based on Gauss-Newton methods (Edgarand and Himmelblau, 1989; Hanna and Sandall, 1995) is used. The optimization procedure depends on the selection of an error function, in order to fit experimental equilibrium data to the isotherm and kinetics models (HO et. al., 2001). The choice of error function can affect the parameters derived – error functions based primarily on absolute deviation bias the fit towards high concentration data and this weighting increases when the square of the deviation is used to penalize extreme errors. This bias can be offset partly by dividing the deviation by the measured value in order to emphasis the significance of fractional deviations. In this study, four non-linear error functions were examined and in each case a set of isotherm parameters were determined by minimizing the respective error function across the concentration range studied. The error functions employed were as follows:

A derivative of Marquardt's Percent Standard Deviation (MPSD) Marquardt, (1963)

$$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{p}\left[\frac{\left(q_{e,meas} - q_e\right)}{q_{e,meas}}\right]_i^2} \tag{3.10}$$

The Sum of the Squares of the Error (SSE)

$$\sum_{i=1}^{p} \left(q_{e,meas} - q_{e,calc} \right)_i^2 \tag{3.11}$$

A composite fractional Error function (HYBRID, Porter et al. (1999));

$$\frac{100}{n-p} \sum_{i=1}^{p} \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{emeas}} \right] \tag{3.12}$$

The Average Relative Error (ARE): (Kapoor and Yang, 1989)

$$\frac{100}{n-p} \sum^{p} \left| \frac{(q_{e,meas} - q_{e,calc})}{q_{e,meas}} \right| \tag{3.13}$$

Where $q_{e,meas}$ is measured from experiment (mg/g), $q_{e,cal}$ is calculate from theoretical model (mg/g).

3.8 Taguchi: Design of experiment

Taguchi method is used to achieve two main objectives through the design of the experiments.

1. To determine the optimum process parameters values conditions for a phenol-TCAC system.

2. Estimate the percentage contribution of each process parameter in phenol-TCAC batch adsorption system.

The parameter design of the Taguchi method includes the following steps were summazie (Trang and yang, 1998):

a) Identify the quality characteristics and process parameters to be evaluated.
b) Determine the number of levels for the process parameters and possible interactions between the process parameters.
c) Select the appropriate orthogonal array and assign the process parameters to the orthogonal array.
d) Conduct the experiments based on the arrangement of the orthogonal array.
e) Analyze the experimental results using the signal-to-noise ratio and statistical analysis of variance;
f) Select the optimal levels of process parameters.

g) Verify the optimal process parameters through a confirmation experiment.

3.8.1 Selection of orthogonal array OA

The selection of parameters and their level was an important step to design a Orthogonal array (OA). OAs is that array in which, for each level of any one factor, all levels of other factors occurred in equal number of times and hence giving a balanced design. OA was originally developed by Taguchi to control experimental error as compared to other statistical method available for design of experiments. Orthogonal array (OA), L_{25} ($5^{\wedge 5}$), which denotes five parameters (temperature, pH, dose of adsorbent, initial concentration, time) each with five levels, was chosen and each experiment was repeated twice under the same conditions at different times to observe the effects of noise sources in the process. Table 3.3 represents the selected orthogonal array for this study.

3.8.2 S/N ratio: A conceptual approach.

Taguchi approach's based on the analysis of loss function which is used to measure the performance characteristics deviating from the experimental value. The value of the loss functions is further transformed into a signal-to-noise (S/N) ratio. Usually, there are three categories of performance characteristics in the analysis of the S/N ratio.

Minimum /smaller is better is given by

$$S/N_i = -10 \log\left(\frac{1}{n}\sum_{j=1}^{n} y_{ij}^2\right) \tag{3.14}$$

Maximum /Larger is better is given by

$$S/N_i = -10 \log\left(\frac{1}{n}\sum_{j=1}^{n} \frac{1}{y_{ij}^2}\right) \tag{3.15}$$

Table 3.2 Orthogonal array L_{25} ($5^{\wedge 5}$) from Minitab 14.

Temp (℃)	**pH**	**Dose (g)**	**Concentration (mg/l)**	**Time (min)**
36	2	1	50	15
36	4	2	100	30
36	8	3	150	180
36	10	4	200	840
36	12	5	400	1440
41	2	2	150	840
41	4	3	200	1440
41	8	4	400	15
41	10	5	50	30
41	12	1	100	180
51	2	3	400	30
51	5	4	50	180
51	8	5	100	840
51	10	1	150	1440
51	12	2	200	15
56	2	4	100	1440
56	5	5	150	15
56	8	1	200	30
56	10	2	400	180
56	12	3	50	840
60	2	5	200	180
60	5	1	400	840
60	8	2	50	1440
60	10	3	100	15
60	12	4	150	30

Chapter-4

RESULTS AND DISCUSSION

4.1 Effect of temperature on adsorbent preparation.

It was clearly shown in Fig. 4.1 that the adsorption of phenol significantly increased as the adsorbent temperature was increased from 400 to 600 ℃, thereby increasing the removal efficiency of phenol. This may be due to the formation of well developed mesopores structures on the adsorbent during activation. This percentage yield can be calculated by equation by (4.1) and was obtained 30.29%. An increased in carbonization temperature the percentage of volatile matter decreased along with yield. Decrease in yield of adsorbent is due to rapid carbonization occurring in (400-800℃) this region. (Bouchelta et. al., 2008) also suggested that it is unsuitable to prepare activated carbon when carbonization temperature was more than 800℃. Since, the successive decreased in volatile matter is minimal. Hence, 600 ℃ is the optimum condition for developing mesopores. The effect of holding time of carbonization is another factor described by (Joseph et. al., 2007 and Bouchelta et. al., 2008). Hence it is preferred to have the fast pyrolysis steps i.e. at heating rate 20℃/minute.

$$\%\ yield = \frac{W_{CHAR}}{W_{RAW}} * 100 \qquad (4.1)$$

Where W_{CHAR} the weight of char obtained after pyrolysis is, W_{RAW} is weight of dried raw material.

4.2 Characterization of the adsorbents

The various properties of the adsorbent produced from waste material of TC's fruits are given in Table 4.1. The CHNS analysis indicates that the activation thus decreased the nitrogen content by typically lower than 1wt. %. Such an amount is lower than what can be found in N-enriched carbons; examples are given in (Laszlo et al., 2001). However, the present material is significantly cheaper in term of cost. In contrast, even if the resultant performances of phenol adsorption are expected to be lower, such TCAC may have a great economic interest. The SEM images of TCAC in Fig. 4.2 and 4.3, in the first image (Fig. 4.2a, 4.2b) was taken at an 1000X magnification and it showed the heterogeneous distribution of pores and formation of rough texture at 450 ℃.

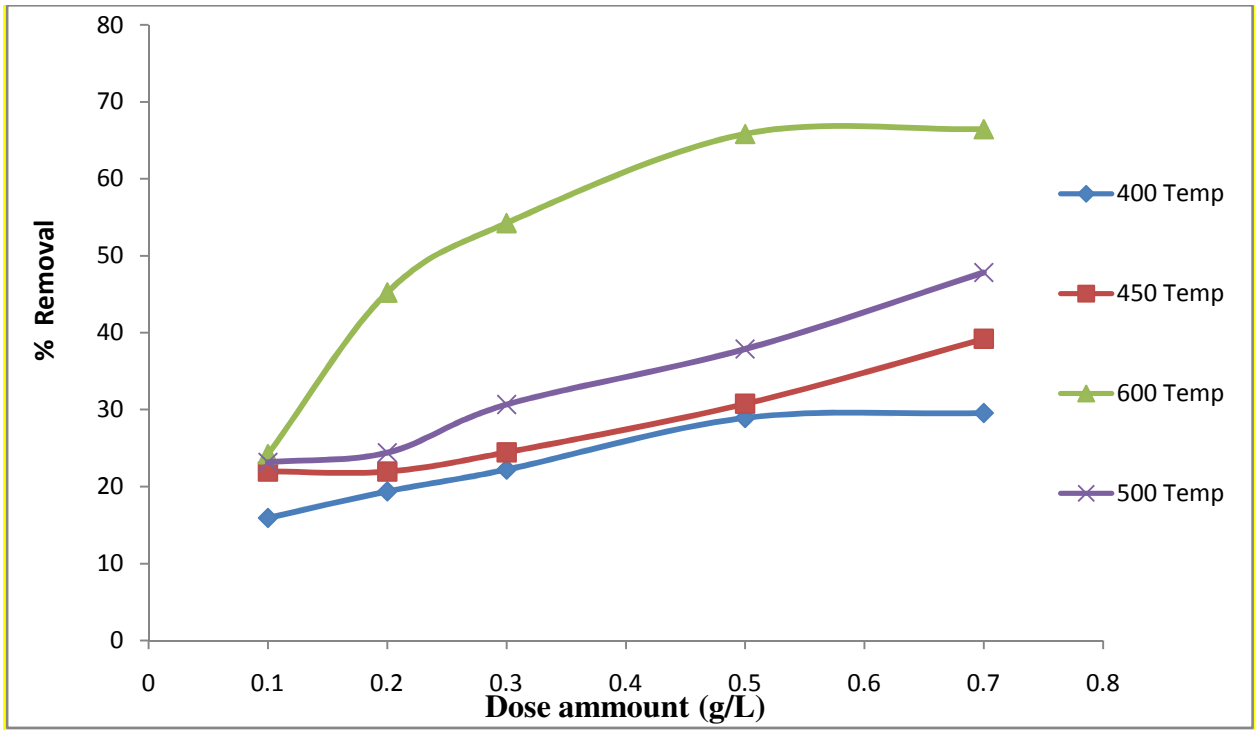


Fig. 4.1 Effect of temperature on synthesis condition on the removal efficiency of phenol.

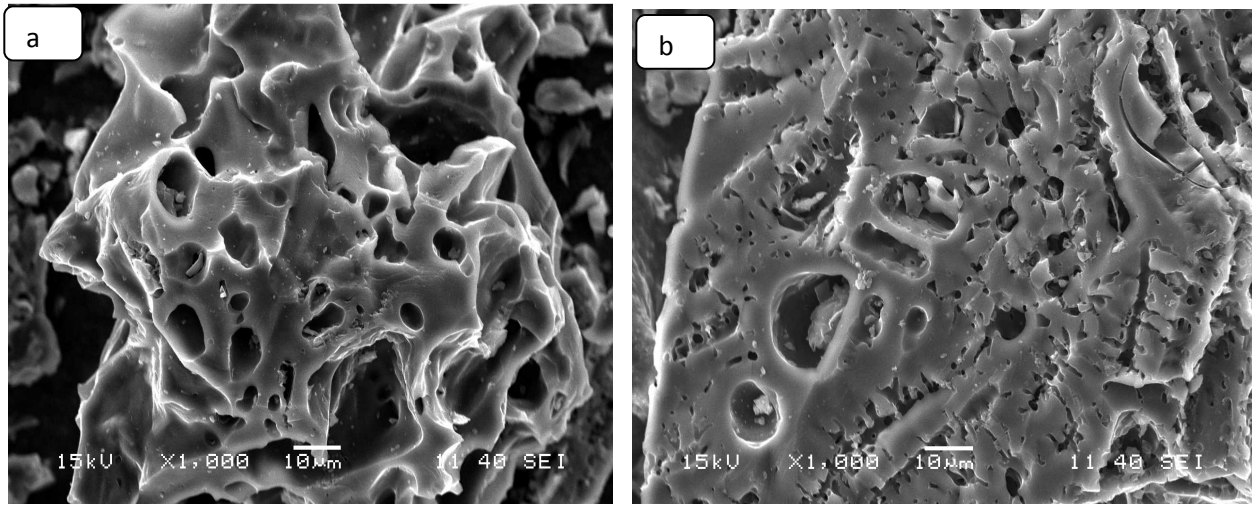


Fig 4.2 SEM images of adsorbent (TCAC) at 1000X magnification prepared at 450℃.

Appearance of white bright spots shows the presence of residual ash. While in figs. 4.3(a, b, c and d) was taken at different magnification. The pore openings at low magnification in Fig. 3a shows that pore of the surface bubble out, describing a sudden burst due to rapid thermal expansion. Further at higher magnification (figs. 4.3b, 4.3c and 4.3d), The high temperature

treated raw material for adsorbent resulted well developed mesopores structures in heterogeneity and pore size distribution at temperature 600℃ (Girods et al., 2009). The pores build-up was found to be very clear opening that provide accessibility into internal pores in Fig. 4.3d at 5000X magnification with no clogging pores. The chemical characterization of TCAC surface was preformed through FT-IR analysis.

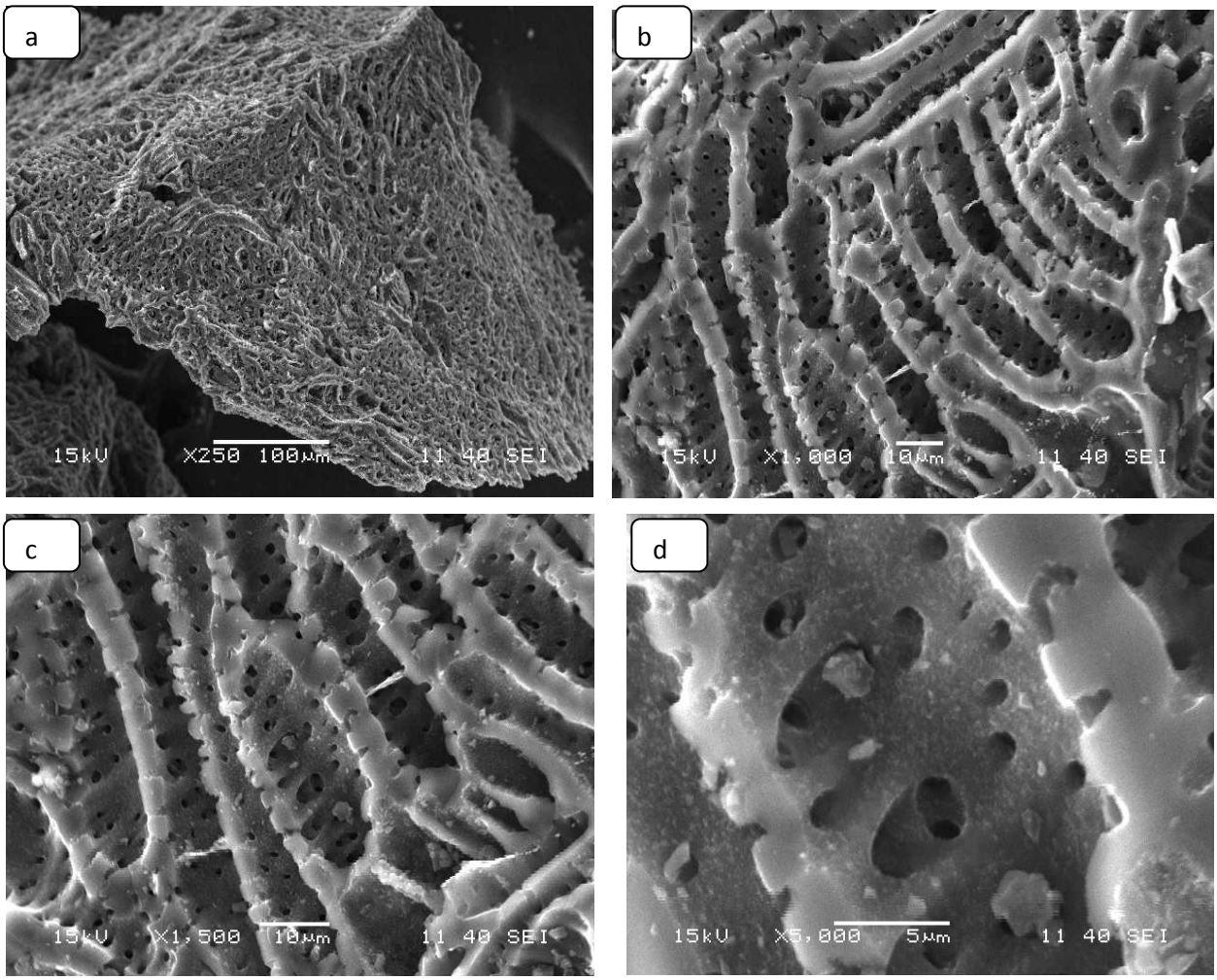


Fig.4.3 SEM images of TCAC prepared at 600 ℃ at different (250X, 1000X, 1500X and 5000X) magnification in 4.3a, 4.3b, 4.3c and 4.3d respectively.

The surface functionality of adsorbent can be characterized by FTIR spectra (Fig. 4.4) where several peaks were obtained. It was found that the band characteristic of the carbonyl functional groups in different surroundings (1650–1500 cm^{-1}) increases considerable in relation to the thermal-vacuum treated sample (Pakuła et al., 2005). The peak in range (1664-1536 cm^{-1}) indicates the presence of carbonyl groups. The appearance of small absorption bands in the 850–

700 cm^{-1} region can be described as C-H out-of-plane bending characteristic of various substituted benzenes

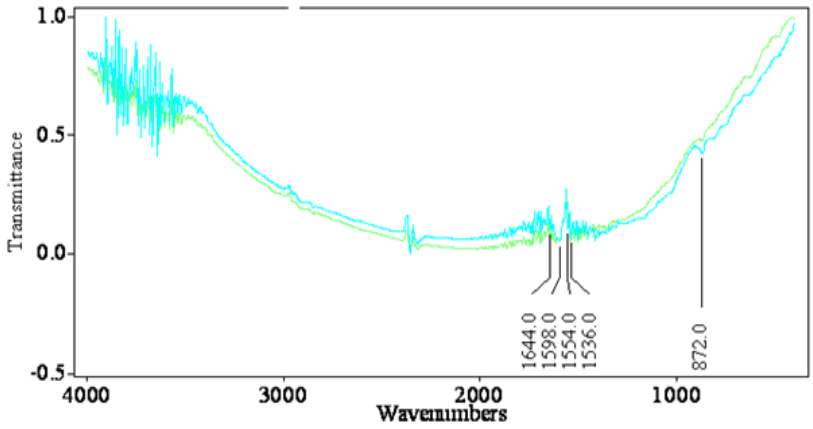


Fig. 4.4 FT-IR spectra of TCAC loaded and virgin (the upper curve was loaded TCAC while lower one is virgin).

Table 4.1 Different properties from CHNS analysis, EDX and BET surface area of TCAC.

ANALYSIS	PROPERTIES
BET surface area	364 m^2/g
Langmuir surface area	413 m^2/g
EDX	
Elements	**Weight Percent**
Carbon	86.19
Oxygen	12.06
Calcium	1.74
CHNS	
Carbon	82.86
Hydrogen	2.697
Sulphur	0.046
Nitrogen	0.55
Oxygen	13.847
TOTAL	**100**

The band near 872 cm^{-1} is characteristic of the radial, skeletal vibration of adsorbed phenol molecules (Coughlin and Ezra, 1968). Similar FT-IR spectral changes were observed during phenol adsorption. The peak shifting was occurred at 872 cm^{-1} which was due to the adsorption of phenol on C-H.

4.3 Effect of adsorbent dose

In order to study the effect of adsorbent dosage, different dosages of TCAC were varied from 1 to 7 g/l, and were placed into series of the 100mL flasks of Phenol solution (100mg/l). These samples were agitated for 24 h at 120 rpm at the neutral pH. A plot of qe and percentage removal was plotted on same axis against adsorbent dose. It was found that with increase in adsorbent dose the percentage removal increases indicating the presence of large surface area available for adsorption with decreasing the maximum adsorption capacity. Hence, the optimum dosage was considered where these intersect Fig.4.5. Hence, in all the experiments, 3 g/l was kept as an adsorbent dosage.

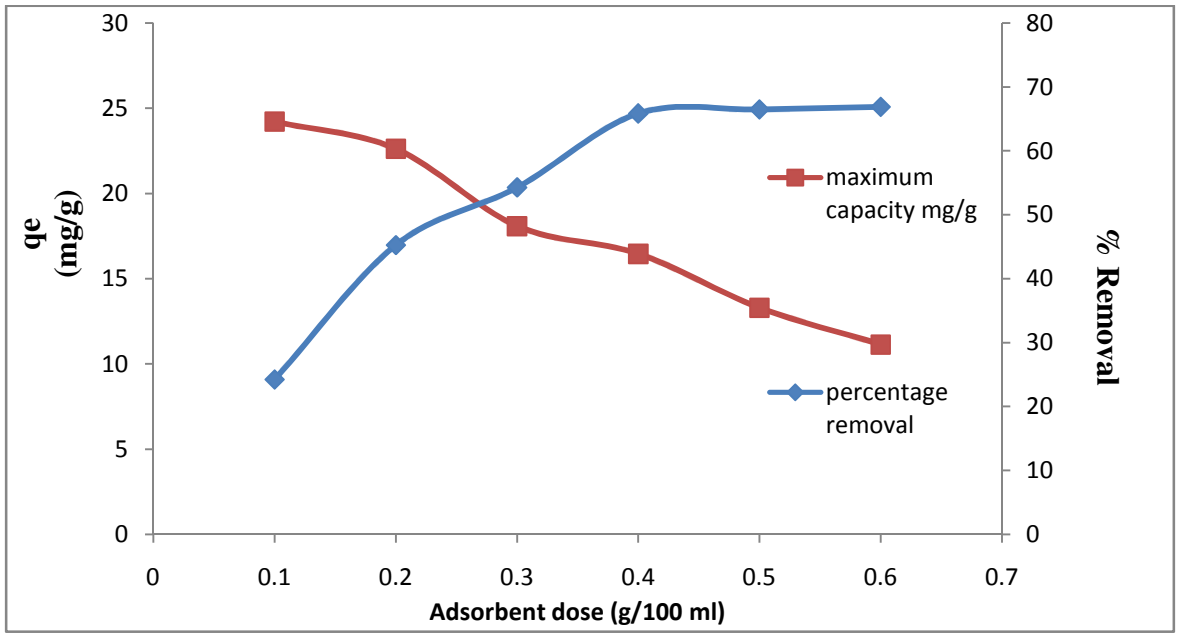


Fig. 4.5 Effect of dose for phenol removal at pH (neutral) 100 mg/l for 24 hours at 30 ℃.

4.4 Effect of initial pH

It is well known that phenol adsorption onto activated carbon can occur via a complex interplay of electrostatic and dispersion interactions with three possible mechanisms (Coughlin and Ezra, 1968)

- $\pi - \pi$ dispersion interaction between the phenol aromatic ring and the delocalized л electrons present in the aromatic structure of the graphite layers.
- Hydrogen bond formation.
- Electron donor–acceptor complex formation at the carbon surface

Although in adsorption process electrostatic attraction exists between phenolate ion (C_6H_5O-) and adsorbent surface as described by (Nabais et al, 2009) in their work, played a very significantly role (and the oxygen of the surface carbonyl group acts as the electron donor and the phenol aromatic ring as the acceptor (Mattson, et al., 1969). Both aspects are determined by the solution pH (Nabais et. al., 2009). Due to the amphoteric character of a carbon surface, its adsorption properties may be influenced by the pH value of the solution (Laszlo et. al., 2003). The effect of initial pH on the adsorption of phenol was also evaluated at 30 ℃ at different initial pH values in the range of 2–12 for initial concentrations of 100 mg/l for phenol solution by adding 0.1M HCl or 0.1M NaOH. The equilibrium uptake as a function of pH for phenol solution water, shown in Fig. 4.6, indicates that higher uptake is achieved for unbuffered Phenol-water. The increased in phenol adsorption was occurred at 5.5 due to the mild increased in H+ adsorption on the carbonyl sites, which suppresses phenol adsorption on these sites. On the other hand, the decrease in the phenol amount adsorbed as the pH increased from 10 to 13 is attributed to both greater solubility of dissociated phenol at pH> pKa and increased repulsion forces between the dissociated form of the adsorbate and the carbon surface (El-Naas et al. 2010).

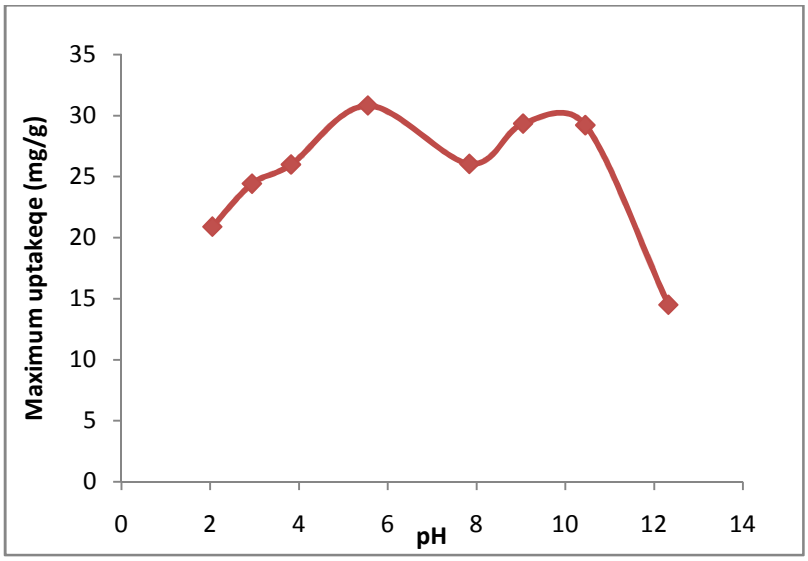


Fig. 4.6 Effect of pH on adsorption capacity in 24 hours at 100 mg/l concentration for 24 hours at 30 ℃.

4.5 Effect of contact time and initial Phenol concentration

To elucidate the effect of initial phenol concentration (100 mg/l), the experiments were carried out different conical flasks with adsorbent dose (3 g/l). These flasks were agitated in shaker for 15, 30, 60, 210, 720, 1440 minutes keeping 5.5 pH fixed in all the samples. The samples were withdrawn from the water bath shaker at predetermined time intervals. The

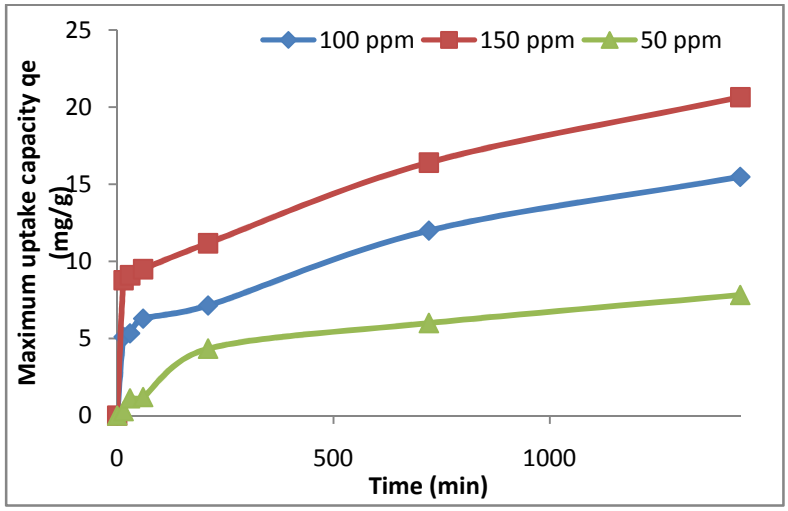


Fig. 4.7 Effect of contact time and initial concentrations on the adsorption of phenol onto TCAC.

Phenol solution was separated out from the adsorbent filtering with 0.45 µm whatman Millipore filter. The concentration of supernannte was measured for all the samples. A graph was plotted with q_e versus time as shown in Fig. 4.7. The q_e was calculated out by equation (2.1). The adsorption data for the uptake of phenol versus contact time at different initial concentrations is presented in the results showed that equilibrium time required for the adsorption of phenol onto TCAC was 1440 minutes (24hours). However, the results also indicated that up to 50% of the total amount of phenol uptake was found to occur in the first (30min) and thereafter the rest 50% of maximum uptake was reached in 24 hours. The uptake capacity increased with increase in initial concentration, which may be due to the availability of more number of phenolate ion in solution for sorption. Moreover, higher initial adsorbate concentration provided higher driving force to overcome all mass transfer resistances of the phenolate ions from the aqueous to the solid phase resulting in higher probability of collision between adsorbent and the active sites (srivastav et al., 2006). The higher sorption rate at the initial period (first 30min) may be due to an availability of large number of vacant sites on the adsorbent at the initial stage, as a result there was an increased in concentration gradients between adsorbate in solution and adsorbate on adsorbent surface. Thus tends to increase in phenol sorption at the initial stages. As time precedes this concentration is reduced due to the accumulation of phenol particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 30 to 1440 min. It is also seen that an increase in initial concentration resulted in increased phenol uptake.

4.6 Effect of temperature

The analysis of surface loading with increase in temperature, Phenol solution was prepared in five different conical flasks with phenol concentration (50, 100, 150, 200, 250 mg/l) and adsorbent dose (3g/l and put inside the water bath shaker. The temperature was maintained at 30℃. The final Phenol concentration was measured after 24 hours. The similar experiments were conducted for temperatures 40℃, 50℃ and 60℃. A plot of uptake capacity of TCAC against time at different temperatures was plotted. It is evident from Fig. 4.8 that the value of maximum adsorption capacity qe decreases with temperature thus suggesting that adsorption is favored at lower temperatures. At high temperature kinetic energy of adsorbate phenol is so high that they do not bind with the active sites available on the TCAC surface. However if the process was endothermicc in nature than only the sorption capacity wolud increase because of inter molecular pore diffusion (weber, 1972).

4.7 Equilibrium kinetics studies

The kinetics describes the solute uptake rate and which controls the residence time for the Phenol-TCAC system. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process (Srivastava et al., 2006). The complaisance between experimental data and the model predicted values was expressed by correlation coefficients (R^2) and the error analysis was performed to know the best suitable of kinetic model.

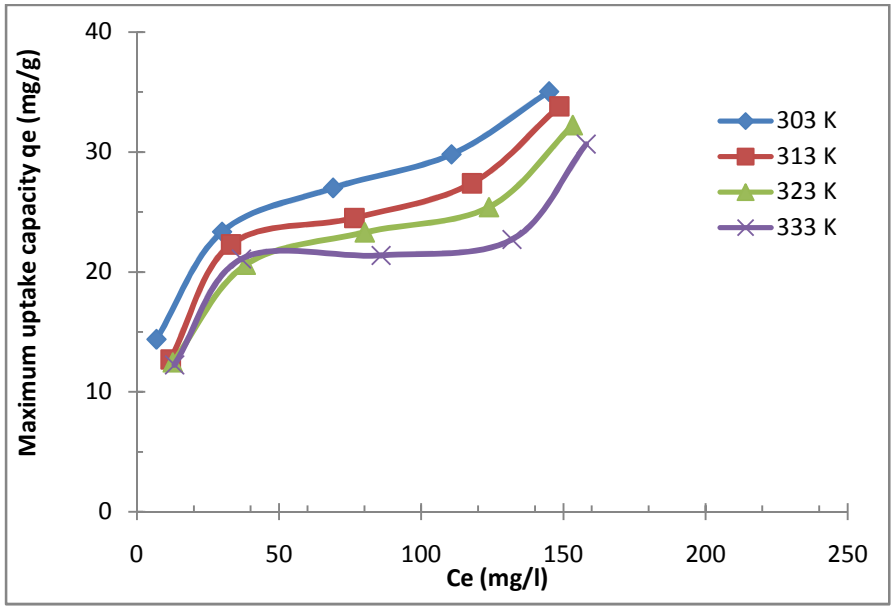


Fig. 4.8 Effect of surface loading of TCAC with temperature at (pH 5.5, t= 24 hours, m 3g/l).

A pseudo-first order kinetic model as below. The integrated form of the Lagergren model by equation (2.3).

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303} t \qquad (4.1)$$

The values of the adsorption rate constant (k_1) for Phenol-TCAC system were determined from the plot of $\log(q_{eq} - q)$ against t was shown in Fig.4.9. The values of q_{eq} and k_1 respectively were given in Table 4.2 for the different initial concentration for phenol solution.

The pseudo-second-order model can be expressed by equation 2.5 where k_s is the pseudo-second- order rate constant (mg/min). Integrating the above equation from t=0 at q_t =0, the linear form of 3.6 equation after rearrangement is given in equation 4.2

$$\frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{1}{q_{eq}} t \qquad (4.2)$$

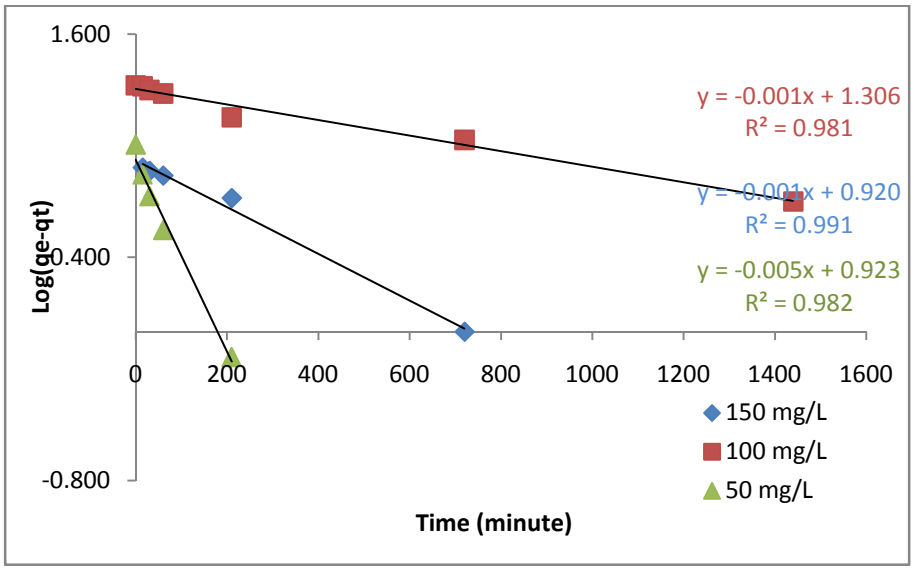


Fig. 4.9 Pseudo-first-order kinetic plot for the Phenol-TCAC system, (T= 303K, m = 3g/l).

The initial adsorption rate, h (mg/gmin), at $t \to 0$ is given by (Srivastava et al, 2006)

$$h = k_s q_e^2 \qquad (4.3)$$

The value of h, k_s and q_e were determined from the slope and intercept of plot $\frac{t}{q_t}$ versus t given in Fig. 4.10 and were listed in table 4.2

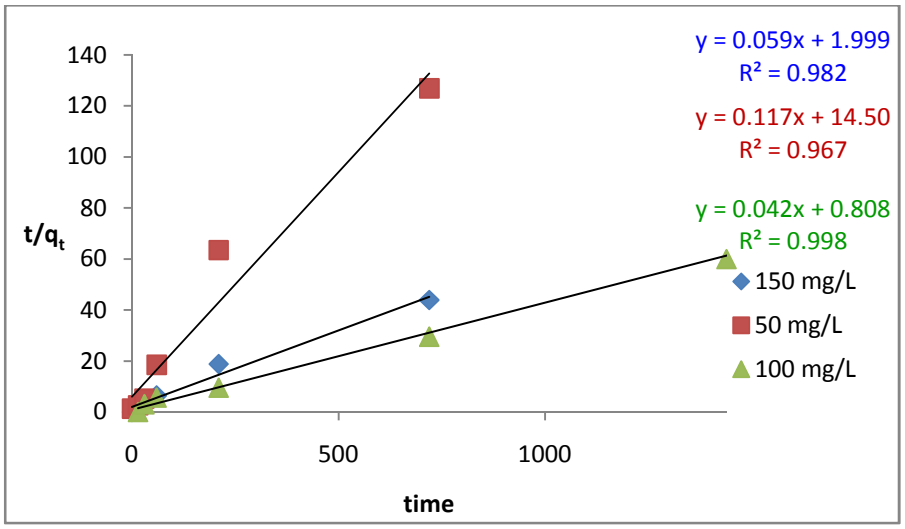


Fig. 4.10 Pseudo-second-order kinetic plot for the Phenol-TCAC system, (T= 303K, m = 3g/l).

Bangham's equation (Aharoni et al., 1979) is given by equation 4.4 gives the idea about the diffusion is the rate-controlling stepin adsorption, which indicates the diffusion of adsorbate into the pores of the sorbent. The double logarithmic plot, according to equation. (4.4), did not yield satisfactory linear curves for the Phenol-TCAC system, (Tutem et al., 1998).

$$\log\log\left(\frac{C_0}{C_0 - q_t m}\right) = \log\left(\frac{k_0 m}{2.303V}\right) + \alpha \log(t) \qquad (4.4)$$

Where V is the volume of the solution (ml), α and k_0 is constants.

The correlation coefficient from equation (4.1-4.4) did not give the clear cut picture about the best suited model. Hence we have to perform the error analysis. Thus the best suited kinetic model is decided by the combining effect of error and correlation coefficient. The MPSD error analysis revealed that each concentration pseudo-second order model was best suited among all the kinetic model equations. While Bangam equation was very poor R^2 value, thus indicated that concept of pore diffusion was not supported for Phenol-TCAC system.

Table 4.2 Kinetic parameters for the removal of phenol by TCAC (T = 303K, C_0 = 50, 100 and 150 mg/l, m =3g/l)

Pseudo-first-order model $q_t = q_e[1-\exp(k_f * t)]$				Error analysis	
C_o (mg/l)	$q_{\exp}$	q_{cal}	k_f	R^2 **(linear)**	**MPSD**
50	11.3458	8.3753	0.0115	0.9822	306.66
100	26.2271	20.2302	0.0023	0.9810	192.61
150	16.4060	9.7949	0.0023	0.9960	148.31
Pseudo-second-order model: $q_t = tk_s q_e^2 / (1+tk_s q_e)$					
C_o(mg/l)	q_{ecalc} **(mg/g)**	k_s **(g/mgmin)**	***h***	**R_2^2(linear)**	**MPSD**
50	11.3458	0.0002	0.0221	0.9670	70.4828
100	26.2271	0.0002	0.1099	0.9980	107.2700
150	16.4060	0.0017	0.5003	0.9820	37.5232
Bangam Equation model					
C_o (mg/l)	k_0 **(g/mg min)**		**α**	**R_2^2 (linear)**	**MPSD**
50	0.24725000		0.5740	0.9690	69.9200
100	0.38649440		0.5050	0.9170	2.9300
150	1.5601		0.2200	0.9110	10.2100

4.8 Adsorption equilibrium study

The several adsorption isotherm models like Langmuir, Frendulich, Temkin, Redlich-peterson and D-R have been used to test the equilibrium kinetics data. (Zeldowitsch, 1934), The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The Freundlich 1906, presented the empirical model which can be applied to non-uniform sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by the following equation 4.5

$$q_e = K_f C_e^{1/n} \tag{4.5}$$

Which could be linearized to Freundlich isotherm and it was often criticized at low concentrations due to the lacking a fundamental thermodynamic basis since it does not reduce to Henry's law (Zeldowitsch, 1934).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4.6}$$

In 1916 Langmuir developed a theoretical equilibrium isotherm and had described good agreement with a wide variety of experimental data and may be represented in equation 4.7

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4.7}$$

At low adsorbate concentrations it effectively reduces a linear isotherm as such in equation 4.8 and thus follows Henry's law. While on the other hand, at high sorbate concentrations, it predicts a constant monolayer uptake capacity.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{4.8}$$

The R–P isotherm (Redlich and Peterson, 1959) can be described in equation 4.9 where K_R is the R–P isotherm constant (L/g), aR the R–P isotherm constant (L/mg) and β the exponent which lies between 0 and 1, C_e the equilibrium liquid phase concentration (mg /L).

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{4.9}$$

For high concentrations, Eq. (4.9) reduces to the Freundlich isotherm, Where $K_f = \frac{K_R}{a_R}$, and $\frac{1}{n} = (1 - \beta)$. While at β=1 equation 4.9 reduces to Langmuir isotherm (Srivastava et. al. 2006).

The Temkin isotherm (Temkin and Pyzhev, 1940) as given in equation 4.10

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (4.10)$$

It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B1 and K_T from the slope and the intercept, respectively. Where B_T = RT/b , q_e (mg/g) and C_e (mg/l) are the amount of adsorbed Phenol per unit weight of adsorbent and unabsorbed Phenol concentration in solution at equilibrium, respectively. A_T and B_T are the Temkin constants. Using, MS Excel, WINDOWS, 2007, The Freundlich, Langmuir, R–P and Temkin isotherm constants were determined from the plots of ln q_e versus $\ln C_e$, C_e/q_e versus Ce $K_R C_e/q_e$ versus $\ln C_e$ and q_e versus $\ln C_e$, respectively, at 303, 313, 323and 333K and the values were reported in table 4.2. Freundlich constants, K_f and $1/n$ indicate the adsorption capacity and adsorption intensity, respectively. Higher the value of $1/n$, the higher will be the affinity between the adsorbate and the adsorbent, and the heterogeneity of the adsorbent sites. The $1/n$ value indicates the relative distribution of energy sites and depends on the nature and strength of the adsorption process. For example, $1/n$=0.36 refers to the fact that 36% of the active adsorption sites have equal energy level. Since $1/n < 1$, Phenol is favorably adsorbed by TCAC at all temperatures. The surface heterogeneity is due to the existence of crystal edges, type of cations, surface charges.

Comparison of the fit of various isotherm equations for the adsorption Phenol-TCAC system at temperature 313 K, t=24h. The net effect of these factors is temperature dependent. The Freundlich isotherm does not predict the saturation of the adsorbent surface by the adsorbate. The value of K_f can be taken as a relative indicator of the adsorption capacity of TCAC for a narrow sub-region having equally distributed energy sites for the sorption of Phenol. The magnitude of K_f also showed the lower uptake of Phenol at higher temperatures indicating exothermic nature of adsorption process. The q_m is the monolayer saturation at equilibrium, whereas K_L corresponds to the concentration at which the amount of Phenol bound to the adsorbent is equal to $q_m/2$. This indicates the affinity between the Phenol and TCAC. A high K_L value indicates a higher affinity. The data in Table 4.2 also indicate that the values of q_m and K_L decreased with an increase in temperature confirming the exothermic nature of the overall sorption process.

Table 4.3 Isotherm parameters and regression coefficient for the removal of Phenol by TCAC (C_0 = 50–250 mg/l, m = 3g/l)

Phenol-TCAC system				
Freundlich				
Temp. (℃)	K_f **(mg/g)/(mg/l)1/n**	***1/n***	R^2	
30	8.6380	0.2743	0.9905	
40	5.8310	0.3416	0.9649	
50	5.4611	0.3386	0.9746	
60	6.1092	0.2969	0.9182	
Langmuir				
Temp. (℃)	q_m **(mg/g)**	K_L **(l/mg)**	R^2	
30	36.7700	0.0581	0.9894	
40	36.5764	0.0376	0.9795	
50	34.6908	0.0345	0.9746	
60	30.7703	0.0409	0.9586	
Temkin				
Temp. (℃)	K_T **(l/mg)**	B_1	R^2	
30	1.3976	6.1902	0.9822	
40	0.5236	7.1644	0.9597	
50	0.4822	6.7941	0.9567	
60	0.7246	5.6943	0.8927	
Redlich-Peterson				
Temp. (℃)	K_R **l/g**	a_R **l/mg**	**β**	R^2
30	15.931	2.0860	0.7580	0.9989
40	4.861	0.5346	0.7410	0.9920
50	35.31	6.1473	0.6706	0.9933
60	4.826	0.5328	0.7760	0.9858

4.8.1 Error analysis

In order to find the best suitable isotherm model, the experimental data was employed to four different error functions. The SSE (sum of square errors function) is commonly used but it has a major drawback, since this function was showing a best fit at the higher end of the absolute concentration. This is due to the magnitude of error will increase by squaring the error value and also it increases with increase in concentration. The error function equation has given in material and methods. Although if the error between the experimental value and theoretical model was increases in this situation SAE (sum of absolute error will give the appropriate result. The ARE (average relative error will minimizes the fractional error across the whole range of concentration (Kapoor and yang, 1989), while the HYBRID hybrid error function was developed to improve the fit of SSE at low concentration. This improvement was done by dividing the value at low concentration by the measured value. In addition a divisor was included as a term for the number of degrees of freedom for the system—the number of data points (n) minus the number of parameters (p) within the isotherm equation. Marquardt's percent standard deviation (MPSD) error function (Marquardt, 1963) is similar in some respects to a geometric mean error distribution modified according to the number of degrees of freedom of the system. The values of the error functions are presented in Table 4.4. Comparison of R^2 values for various isotherms for Phenol-TCAC system shows that these values are closer to unity for Langmuir, R–P and Freundlich isotherms. By comparing the results of the values for the error function MPSD and HYBRID (Table 4.4), it can be concluded that the Freundlich isotherms generally best represent the equilibrium data of Phenol onto TCAC. Comparable fit of various isotherm models for the adsorption of TCAC-Phenol system at 303 and 313 K is shown in Figs. 4.09 and 4.10. It is seen that the Freundlich for 303 and 313 K and R–P equations describe best the experimental equilibrium data for high temperature from error function and R^2 value.

Table 4.4 Values of four different error analyses of isotherm models for adsorption of Phenol on TCAC (C_0 =50–250mg/l, m = 3 g/l)

30 ℃	**SSE**	**HYBRID**	**MPSD**	**ARE**
Langmuir	16.4885	2.8803	12.0881	9.7267
Freundlich	3.6303	-0.1917	3.8085	3.8877
Redlich-Peterson	3.5548	-0.3414	3.5596	3.7305
Tempkin	4.7399	-0.0267	3.8496	3.7740
40 ℃	**SSE**	**HYBRID**	**MPSD**	**ARE**
Langmuir	17.432	-0.7598	5.666	5.6344
Freundlich	6.1554	-1.1353	7.0080	5.2114
Redlich-Peterson	45.0050	3.8304	9.5870	9.8724
Tempkin	12.9212	-1.2919	6.4568	5.8538
50 ℃	**SSE**	**HYBRID**	**MPSD**	**ARE**
Langmuir	44.1204	-10.8566	13.2051	13.0279
Freundlich	42.1885	-13.1372	15.9551	15.7646
Redlich-Peterson	42.1645	-13.1485	15.9216	15.7782
Tempkin	43.4609	-13.1606	15.4726	15.7927
60 ℃	**SSE**	**HYBRID**	**MPSD**	**ARE**
Langmuir	152.3083	-24.8118	31.6452	29.7741
Freundlich	151.8668	-27.5175	31.5713	33.0210
Redlich-Peterson	153.2031	-27.6000	32.0833	33.1200
Tempkin	161.3719	-28.4360	33.3470	34.1232

4.9 Thermodynamics study

The thermodynamics study was performed to know the feasibility of the process. The standard enthalpy change was estimated by applying Van't Hoffequation, and equilibrium constant was calculate using (5) (Ucun et. al., 2008).

$$\Delta G^{o}_{ad} = -RT \ln K_{ad} \quad (4.11)$$

$$\Delta G^{o}_{ad} = \Delta H^{o} - T\Delta S^{o} \quad (4.12)$$

From equation 3 and 4 we get

$$\ln K_{ad} = -\Delta H^{o}/RT + \Delta S^{o}/R \quad (4.13)$$

$$K_{ad} = \left[\frac{(C_0)}{C_e}\right] \quad (4.14)$$

Where, ρ is the density of the solution (g/l), ΔGoad the free energy change (expressed in kJ/mol), ΔH^{o} the standard enthalpy change (in J/mol), ΔSo the standard entropy change (in J/mol K), T the absolute temperature (in K), K_{ad} the equilibrium constant of interaction between the adsorb-ate and the TCAC surface, and R is the universal gas constant (R = 0.008314 J/mol K). The value of ΔH^0 for Phenol-TCAC at 303 k and 50 mg/l, adsorption systems were found to be -16.596 J/mol. The values of ΔS° for the respective systems were found to be 5.312 J/mol K, at same conditions, indicating that the adsorption process is exothermic in nature. The positive value of ΔS^0 suggests an increased randomness at the solid–solution interface, and an increase in the degree of freedom of the adsorbed species (Srivastava et al., 2006).

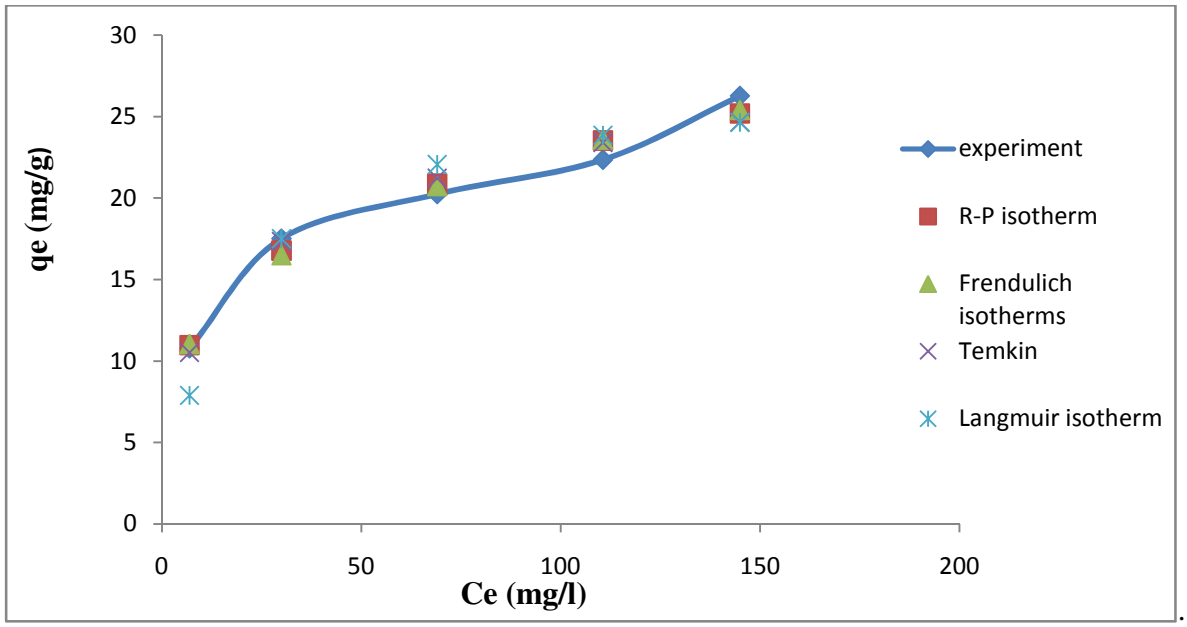


Fig. 4.11. Isotherm plot for the removal of Phenol-TCAC system at T = 303K (t =24 h, m = 3g/l).

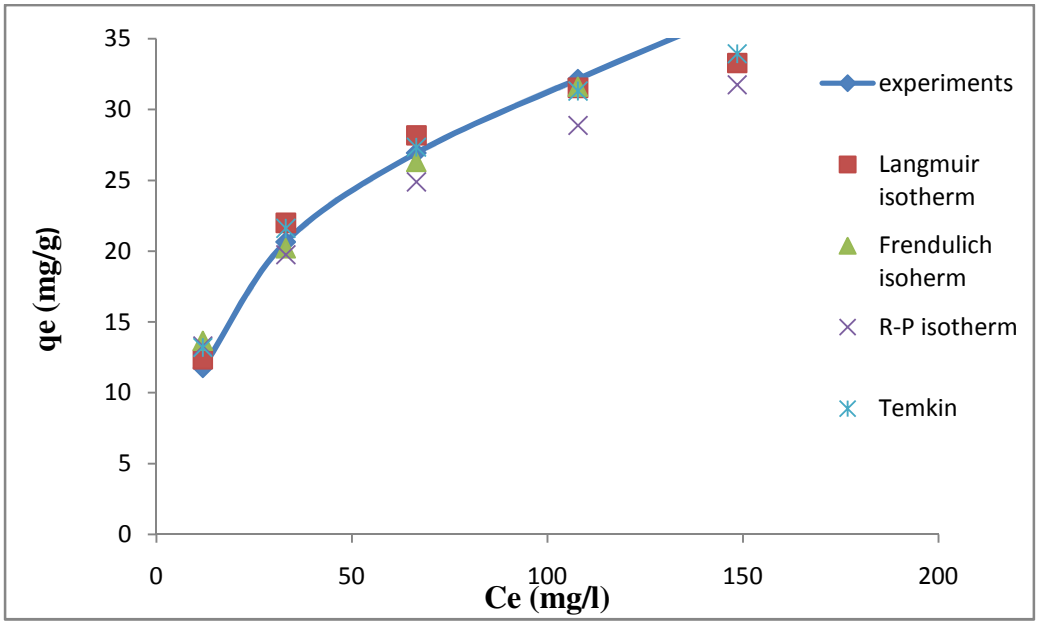


Fig. 4.12. Isotherm plot for the removal of Phenol-TCAC system at T = 313 K (t =24 h, m = 3g/l).

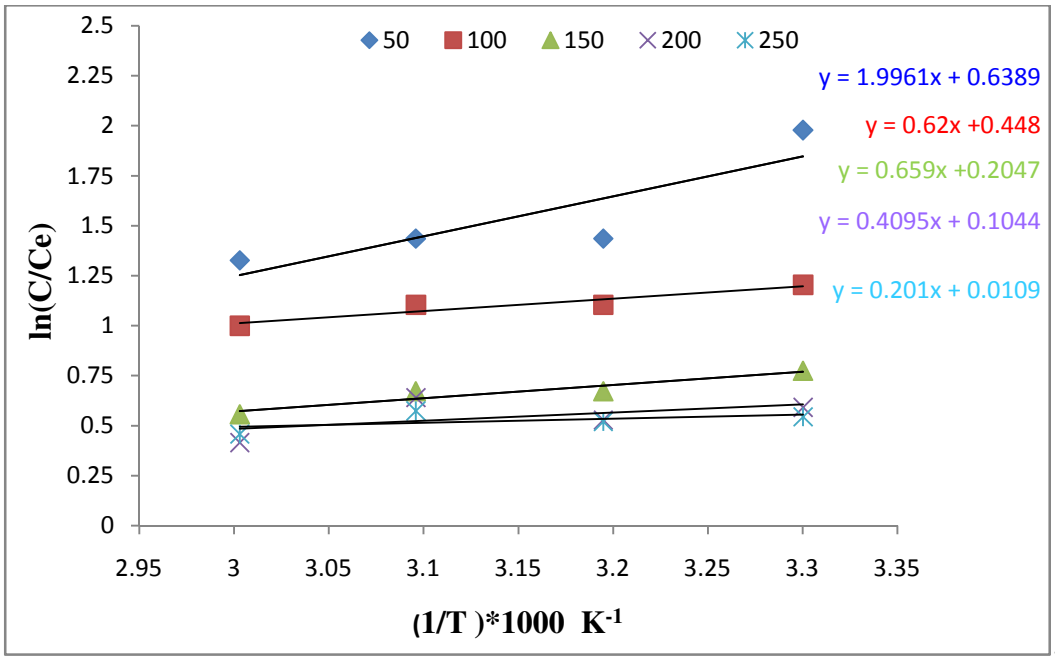


Fig. 4.13 The effect of temperature on the equilibrium distribution coefficient phenol. Initial concentration C_0 = 50, 100, 150, 200 and 250 mg/l (t =24h, m= 3 g/l).

Table 4.5 Thermodymainc results of the batch experiment at different concentration

Concentration	**50(mg/l)**	**100(mg/l)**	**150(mg/l)**	**200(mg/l)**	**250(mg/l)**
ΔH (J/mol)	-16.59545	-5.1055	-5.4788	-3.404	-1.675
ΔS (J/mol K)	5.31185	3.724672	1.701876	0.867982	0.162954
ΔG (J/mol) , 303 K	-1626.086	-1133.681	-521.147	-266.402	-51.05
ΔG (J/mol) , 313 K	-1679.205	-1170.928	-538.166	-275.082	-52.679
ΔG (J/mol) , 323 K	-1732.323	-1208.175	-555.185	-283.762	-54.309
ΔG (J/mol) , 333 K	-1785.442	-1245.421	-572.204	-292.441	-55.938

4.10 Analysis of Taguchi design of experiment.

The experimental data were analyzed by Minitab14 software to evaluate the effect of each parameter on the optimization criteria. Table 3.4 shows the results and corresponding calculated S/N ratio data for phenol removal onto TCAC based on L_{25} ($5^{\wedge 5}$) matrix design. To use the S/N ratio for the minimum for the response performances (table 4.6), S/N calculation was performed and calculated from equation (4.15) to minimize C_e response i.e. the concentration of phenol at time t by TCAC adsorbent from aqueous solution.

The regression equation is

$$C_{cal} = 66.8 + 0.104C_0 - 9.4pH + 0.0019t^2 = 0.676pH^2 + 0.00169C_0^2 - 0.000016t^2$$

$$S/N = -10 * Log\frac{\sum[Y^2]}{n} \qquad (4.15)$$

Where n is the number of experiments, N is error calculate from (C_e-C_{cal}) value.

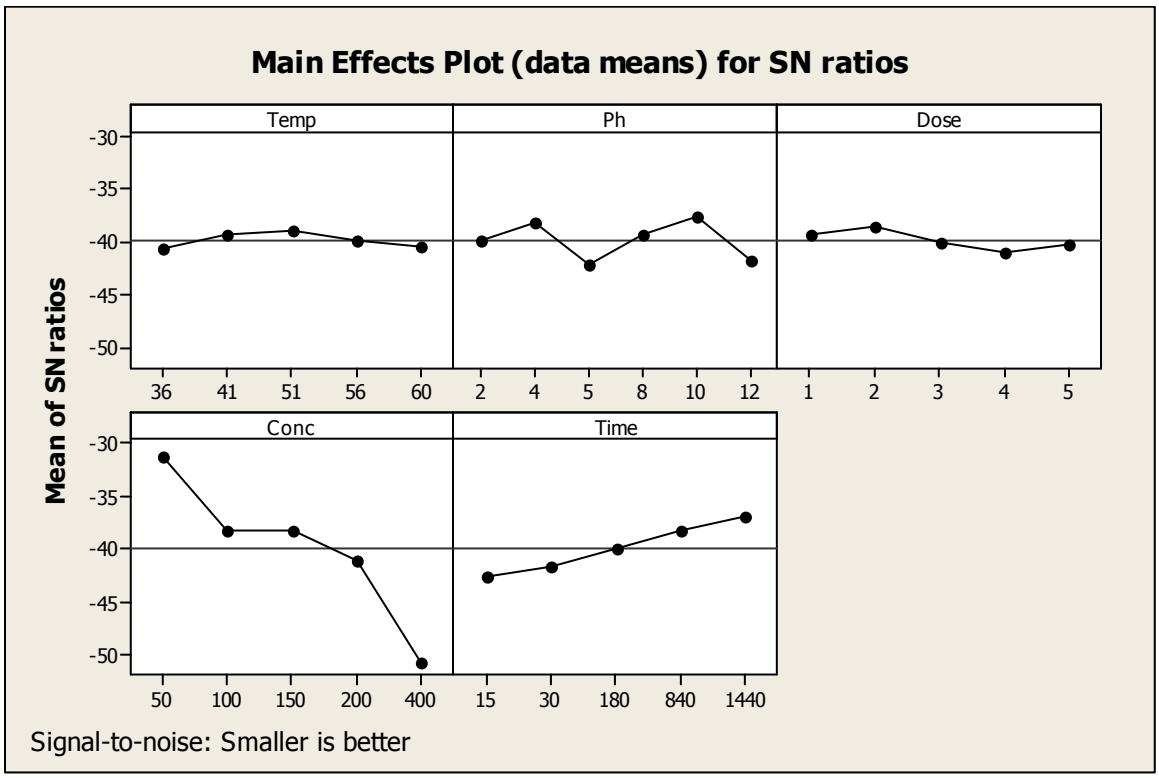


Fig. 4.14 Main effect plots of process parameter Vs S/N ratio.

Table 4.6 S/N ratio value for different experiment parameters using Taguchi design.

Temp	**Ph**	**Dose**	**Conc**	**Time**	**C_e mg/l**	**S/N ratio**
36	2	1	50	15	48.694	-33.7495
36	4	2	100	30	85.981	-38.688
36	8	3	150	180	111.738	-40.964
36	10	4	200	840	92.303	-39.3043
36	12	5	400	1440	362.40	-51.1838
41	2	2	150	840	56.856	-35.0955
41	4	3	200	1440	77.569	-37.7938
41	8	4	400	15	392.00	-51.8657
41	10	5	50	30	42.755	-32.6197
41	12	1	100	180	91.228	-39.2026
51	2	3	400	30	389.60	-51.8124
51	5	4	50	180	42.869	-32.6429
51	8	5	100	840	57.463	-35.1878
51	10	1	150	1440	32.056	-30.1182
51	12	2	200	15	191.10	-45.6252
56	2	4	100	1440	85.919	-38.6818
56	5	5	150	15	123.938	-41.8641
56	8	1	200	30	123.938	-41.8641
56	10	2	400	180	219.767	-46.8392
56	12	3	50	840	32.056	-30.1182
60	2	5	200	180	106.731	-40.5658
60	5	1	400	840	398	-51.9977
60	8	2	50	1440	22.113	-26.893
60	10	3	100	15	99.131	-39.9242
60	12	4	150	30	139.788	-42.9094

The results of analysis of variance (ANOVA) are given in Table 4.8. Statistical analysis of variance was performed to check whether the process parameters are statistically significant or not. The F-value for each process parameter indicates which parameter has a significant effect on the Phenol removal and is simply a ratio of the squared deviations to the mean of the squared error. Usually, the larger the F-value (F>4) has the greater the effect on the Phenol removal. Optimal conditions for the process parameters can be predicted using ANOVA analysis and performance characteristics (Phadke, 1989).

The results of ANOVA analysis for the removal of Phenol onto TCAC is given in Table 4.7. Larger the F-value more is the effective parameter in the Phenol uptake. The sequential order of the process variables is C_o >t> pH >dose >T for Phenol removal onto TCAC.

The degrees of the influences of parameters on Phenol removal are given at the graphs in Fig.4.13. The optimal level of a process parameter is the level with the highest S/N ratio. At first sight, it is difficult and complicated to deduce the experimental conditions for the data given in figure. Let us consider with parameter temp. Now, let us try to determine the experimental conditions for the first data point. The temperature for the serial no 1-5 is 31 ºC. The experimental conditions for the second data point 5-10, are those for which its temperature is 41 ℃ (i.e. experiments nos. 6, 7, 8, 9, and 10), and so on. The numerical value of the minimum point in each graph marks the best value of that particular parameter (Table 4.6). The adsorbate initial concentration had the most important effect on the phenol removal process, because, with the increase of the phenol concentration in aqueous solution, the rate of removal of phenol is increased. The results also showed that at high temperature (36℃), reduces the rate of Phenol removal. It is desired that low temperatures must be selected for higher removal. From Fig. 4.13 Contact time between adsorbate and adsorbent shows that there is high enough fluctuation in S/N ratio, so it provides very high flexibility for selecting contact time. If the experimental plan given in Table 4.6 be studied carefully. It can be observed that the conditions corresponding to optimum conditions for highest Phenol uptake onto TCAC and these are pH=5 t= 15-30 min, T= 36℃ and C_o= 400 mg/l. The interaction between various parameters had also been in Fig.2. Which indicates that the interaction between dose, pH, and time in ranges from (3-4 g/l), 200-400 mg/l, and 15-30 min were the best possible range of parameters for experiment study This contour plots were drawn using Mini TAB 14 software.

Table 4.7 Analysis of Variance (ANOVA) for C_e, using Adjusted SS for Tests

Source	**DF**	**Seq.SS**	**SS. Adj**	**F**
Temp	4	3611	5989	1.32
Ph	5	28400	17156	3.04
Dose	4	3457	3005	0.66
Conc	4	293106	287981	63.69
Time	4	15261	15261	3.38
Error	3	3391	3391	
R2 coefficient		0.992	0.9219	
Total	**24**	**347225**	**332783.92**	

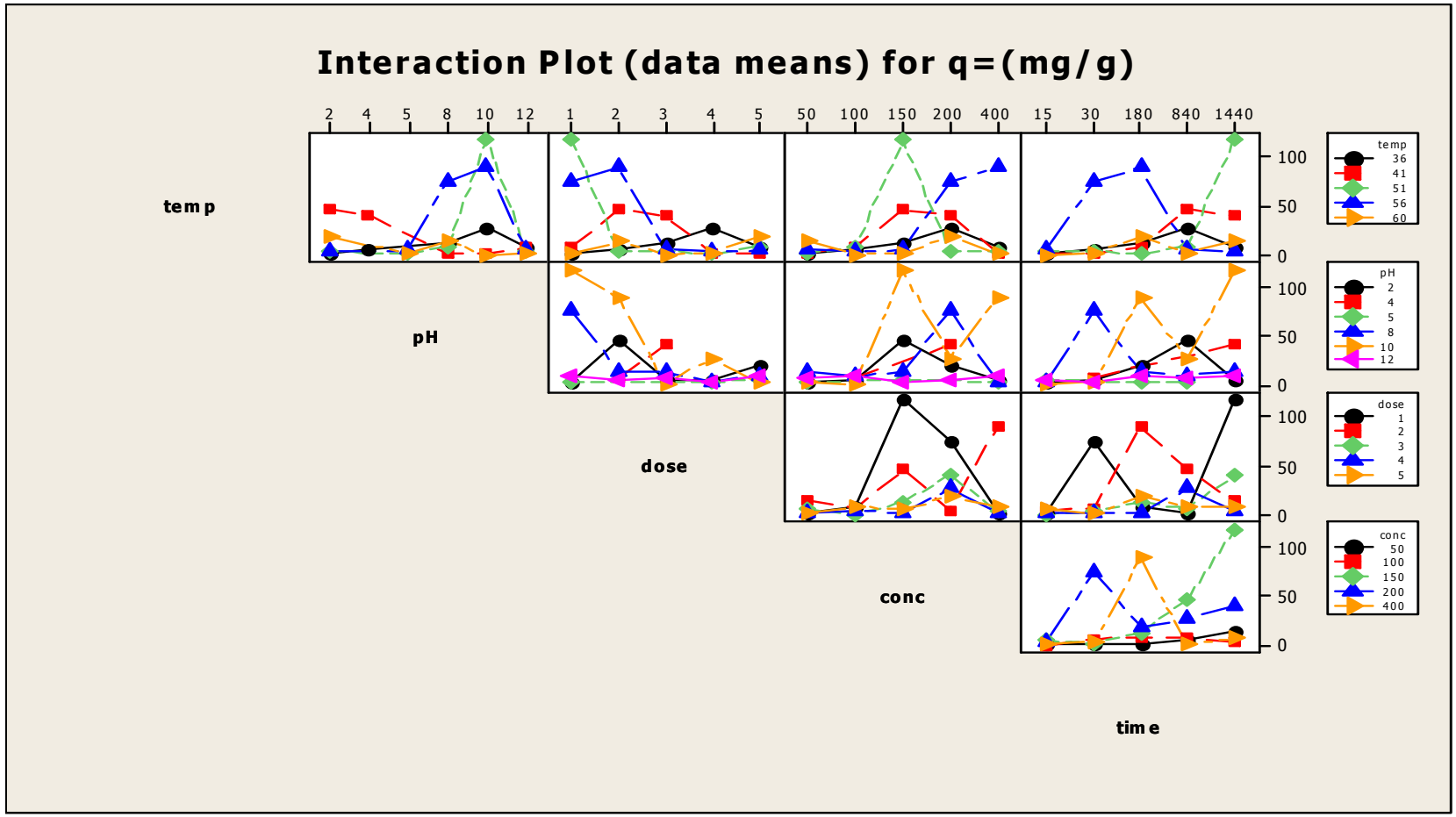


Fig. 4.15 Effect of process parameters and their interaction with each others on maximum uptake value of TCAC-Phenol system

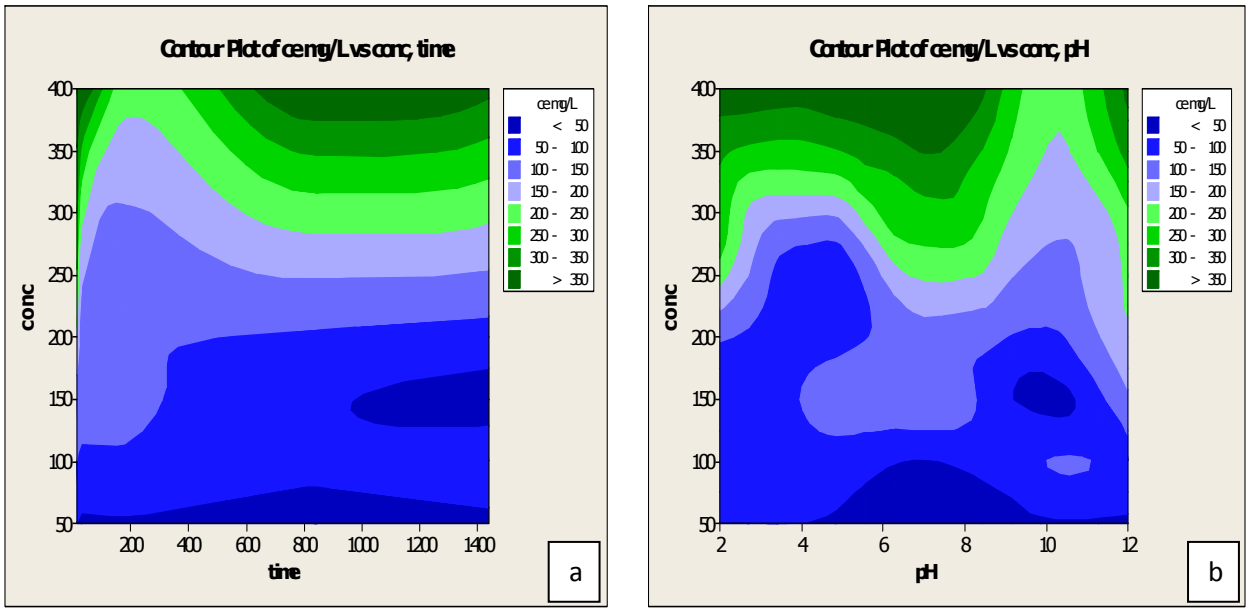


Fig.4.16 (a) contour plot between time, concentration versus C_e ; (b) Concentration, pH versus C_e process parameters for Phenol-TCAC system.

Table 4.8 Comparison of Taguchi approach and univariate technique results.

Process variable	**UNIVARIATE TECHNIQUE**	**TAGUCHI'S APPROACH**
pH	5.5	5
Dose (g/l)	3	3-4
Time (minute)	1440	1440
Initial Concentration (mg/l)	> 150 ppm	<400 ppm
Temperature (°C)	30	36

The comparison of maximum uptake of phenol with laboratory prepared TCAC was shown in table 4.9.

Table 4.9 comparison of adsorbent with commercial activated carbon (Busca et. al, 2008)

Adsorbent	**Solute/ pH**	**T(℃)**	**Model used**	**Capacity (mg/g)**
TCAC (600 °C)	**Phenol/ 5.5**	**30**	**Frendulich**	**36.77**
GAC	Phenol 5.7	–	Langmuir	350
APET	Phenol/ 5	–	Langmuir	262
APET	Phenol / 11	–	Langmuir	184.2
CCM200 (carbon cryogel)	Phenol / –	–	Langmuir	140
G-BAC	Phenol /	–	Langmuir	235.4
PACT (power activated carbon treatment)	Phenol /	25	Langmuir	135.7
Steam-PAC (from coal)	Phenol/	–	–	226
Chemical-PAC (from coal)	Phenol /	–	–	98
GAC (F400) F-DI	Phenol /	–	Freundlich	75.2
GAC(F400) F-HCl	Phenol/	–	Freundlich	75.5
F400-N_2	Phenol/	–	Freundlich	96
F400-Air	Phenol/	-	Freundlich	54
CNTs	Phenol/	-	-	15.9

Chapter-5

CONCLUSION

5 CONCLUSION

The following conclusion can be drawn from the present study

- The maximum uptake of Phenol onto TCAC was found to be 36.77 mg/g.

- t=24 h, pH=5.5, C_o=150 mg/l, T=30 ℃ and m= 3 g/l were the optimum condition for Phenol-TCAC system.

- Over all analysis of equilibrium model and error analysis indicates the fitness of Freundlich model and R-P isotherm.

- Adsorption kinetics was found to follow second order rate expression.

- Adsorption of phenol is decreases with increase in the temperature indicating exothermic nature of the adsorption process.

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Publication from thesis

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APPENDIX

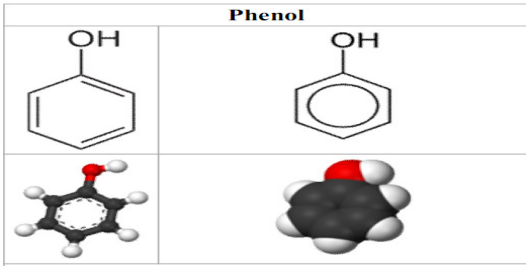
Phenol

What is phenol?

Phenol (C_6H_5OH) is an organic compound and is both a manufactured chemical and a natural substance with a sweet, tarry odor. It ranges from colorless to pink in color. The commercial product is a thick liquid. Natural, pure phenol is a crystalline solid. Synonyms for phenol include carbolic acid, benzophenol, and hydroxybenzene.

Phenol is the preferred chemical for embalming bodies for study because of its ability to preserve tissues for extended periods of time. Phenol:Chloroform Extraction is a common laboratory technique used to isolate DNA, RNA and proteins.

Phenol structure



What are the health effects of phenol?

Exposure to phenol can pose a severe health hazard and should be handled with extreme caution. Phenol is highly corrosive and is readily absorbed through to the skin, whereupon it can affect the central nervous system and cause damage to the liver and kidneys. It is also a mutagen, and there is some evidence that phenol may be a reproductive hazard. When heated, phenol will produce fl ammable vapors that are highly toxic (at just a few parts per million) and explosive (at concentrations of 3% to 10% in air).

Inhalation	• Can irritate the nose, throat, and lungs • Higher exposures may cause a build-up of fluid in the lungs
Oral	• Ingestion of as little as 1 gram can be fatal to humans
Eyes	• Can also cause severe eye damage, including blindness
Skin	• Irritating and corrosive to the skin • Little or no pain may be felt on initial contact due to its local anesthetic effect • Skin contact will cause the skin to turn white; later severe burns may develop • Rapidly absorbed through the skin; toxic or fatal amounts can be absorbed through relatively small areas
Chronic Exposure	• Repeated or prolonged exposure to phenol or its vapors may cause headache, nausea, dizziness, difficulty swallowing, diarrhea or vomiting • Can affect the central nervous system, liver and kidneys
Physical Hazards	• May be combustible at high temperature • Flammable in the presence of open flames, sparks and heat
Exposure Limits (Cal/ OSHA)	• Cal/OSHA: Permissible Exposure Limit (PEL) is 5 ppm for an 8 hour work shift • NIOSH: Short Term Exposure Limit (STEL) is 15.6 ppm for a 15 minute, high exposure activity

How can I protect myself from phenol?

- Work with phenol in a chemical fume hood.
- Never heat or melt phenol in an incubator, microwave, drying oven, autoclave, or similar appliance.
- Review a Phenol Material Safety Data Sheet (MSDS) before handling the material (see UC MSDS website).
- Ensure that there is immediate and unobstructed access to an eyewash/shower unit in your work area.
- As with any chemical, do not eat, drink, or smoke where phenol is handled, processed, or stored.
- Store phenol in a cool, dry, well-ventilated area, away from heated surfaces, ignition sources, strong oxidizers and strong bases.
- Store below eye level to prevent injuries in case of a spill.
- Always wash hands thoroughly after handling phenol, even though gloves are used.

What personal protective equipment (PPE) is required?

PPE: Remember, when working with hazardous chemicals, long pants, closed-toe shoes, safety glasses or goggles are ALWAYS required (see UCLA PPE Policy and EH&S PPE Selection Guide). The following PPE table outlines specifi c requirements for working with phenol.

Gloves and Clothing	• Neoprene gloves when working with only phenol • Double nitrile gloves may be worn when working with phenol:chlorophorm (see note below) • Lab coat
Eye Protection	• For liquid phenol: impact and splash resistant chemical goggles • For solid phenol: eye protection with side shields or goggles
Respiratory Protection	• Respiratory protection must be worn if the ambient concentration of phenol exceeds regulated exposure limits (see table on previous page) • Respirator users must receive an assessment and complete training through the *UCLA Respiratory Protection Program* before using a respirator

What special precautions are needed for phenol:chloroform extractions?

Chloroform is a skin and eye irritant, and it is a suspected human carcinogen and reproductive hazard. Adding chloroform to phenol enhances the ability of phenol to be absorbed by the skin. Also remember that phenol can cause severe burns to the eyes.

- Perform all procedures involving greater than 500 ml of phenol or chloroform or any amount of ether in a chemical fume hood.
- Wash hands thoroughly immediately after removing gloves when working with these chemicals.
- Grasp both the tube and the cap when vortexing to prevent the cap from opening, causing a splash or aerosol.
- Use sealed safety cups when centrifuging phenol:chloroform, and wait at least 10 minutes before opening the centrifuge to prevent exposure to aerosols.
- Segregate pipette tubes/tips from liquid waste.
- Wear chemical splash goggles when there is a splash hazard (for example, when pouring phenol).
- Wear disposable nitrile gloves to protect against accidental hand contact (if accidental contact occurs, remove and discard contaminated gloves immediately).
- The breakthrough time for a 4 ml nitrile glove is approximately 3 minutes for chloroform.
- If a spill occurs, wear Viton or Silver Shield/4H gloves (do not wear nitrile gloves due to the risk of direct or prolonged contact when cleaning up a spill).

Please note: Neoprene gloves are recommended for handling large quantities of phenol where there is risk of accidental splash hazards. If more fi nger dexterity is required, double Nitrile gloves may be worn but users should be aware that glove permeation may occur in several minutes. Change gloves immediately if any liquid contacts your gloves, and frequently during handling of phenol:chloroform solutions.

How do I dispose of phenol waste?

- Handle & dispose of as hazardous waste.
- Phonol is categorized as an extremely hazardous waste, so dispose of empty phenol containers as hazardous waste.